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THE CHEMISTRY AND TECHNOLOGY OF HIGH EXPLOSIVES

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Pages 252 through 567

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Part II
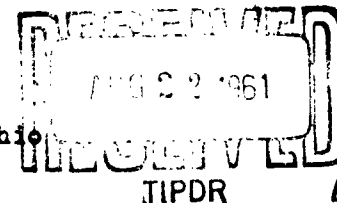
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Section 1. Chemistry of the Production of, Properties of, and Applications of the Nitro Derivatives of Benzene

Benzene is a colorless, highly refractive liquid with a characteristic aroma. Its boiling point is 80.1°, melting point 5.58°, specific gravity $d_{4^{\circ}}^{15^{\circ}} = 0.8787$, $d_{4^{\circ}}^{50^{\circ}} = 0.8454$.

Technical benzene always contains foreign impurities. The major impurities in benzene from coal are sulfur compounds: thiophene (boiling point 84°), which may constitute up to 0.5% of the whole, and traces of carbon disulfide (boiling point 47°).

Thiophene differs from benzene by its capacity vigorously to oxidize nitric acid, and therefore, in the nitration of benzene, additional nitric acid is expended to oxidize the thiophene.

Thiophene and carbon disulfide are usually not present in benzene made from petroleum. However, this benzene does contain a considerable quantity (up to 5%) of gasolines, as well as of unsaturated hydrocarbons.

The following specifications must be met by coal-derived benzene to be used for nitration: specific gravity $d_{4^{\circ}}^{20^{\circ}} = 0.875 - 0.880$; boiling point between
is
$79.0 - 80.6^{\circ}$. The degree of purification determined by the absorption of bromine
titer
(the bromine must not be more than 0.42 per 100 cc benzene), and by the color due to sulfuric acid (not more than 30% of a standard sample). Moreover,

131 not less than 95% of the benzene by volume should distill within 0.8°. The benzene is tested for the presence of these impurities in a manner similar to the testing of the toluene, as described in the section "Trinitrotoluene".

Benzene is difficultly soluble in water: 100 cc water dissolve 0.082 cc benzene
ether,   disulfide,
at 20°. Benzene will mix with alcohol, acetone, carbon

and ligroin,
XXXXXXXX in any ratios. It is a solvent for fats, oils, rubber, nitrocellulose,

etc., and burns with a very smoky fire.

Benzene is toxic, and safety rules must be strictly adhered to in working

with it.

Benzene is transported in iron tank cars. Inasmuch as it has a high

freezing point, it is necessary to thaw frozen benzene in winter. This is

usually done in thawing sheds, in which the temperature of 40 - 30°C is maintained,

and in which the benzene thaws out in 24 - 30 hrs. Other methods of thawing

frozen benzene are also employed.

Mononitrobenzene is formed upon nitration of benzene by nitric acid or

mixed acid, in accordance with the equation

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O.$$
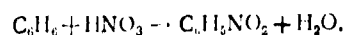
Mononitrobenzene is a yellow liquid smelling of bitter almonds. It boils

at 210.6°, freezes at 5.7°, and its specific gravity is $d_4^{15°}_{0} = 1.204$.

Mononitrobenzene is readily distillable by steam. Its solubility in

sulfuric acid and mixed acid at 43° (Bibl.81) is presented in Table 33.

Table 33

| a)	b)	c)	d)
50	0,02	40—50	about 0,015
60	0,03	60	about 0,02
70	0,04	—	—

a) Strength of H_2SO_4, %; b) Solubility of mononitrobenzene, %; c) Strength of
H_2SO_4, containing 0.2% HNO_3, %;

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Mononitrobenzene dissolves very slightly in water, but well in ether, alcohol, benzene, and strong nitric acid. It is ..self a solvent for ▮▮▮▮ many organic substances, including nitrocellulose, with which it forms a gelatinlike substance. In its chemical properties, it is typical nitrocompound, and yields aniline upon reduction. It dissolves in sulfuric acid, but if undissolved nitrobenzene remains, it can be extracted by anhydrous sulfuric acid out of the acid layer, yielding a compound of the following composition $C_6H_5NO_2 \cdot H_2SO_4$ (Bibl.82).

In the liquid form, mononitrobenzene does not have explosive properties. However, in the gaseous form and in a vessel heated to high temperature under pressure, it is capable of decomposing with great force (Bibl.83).

Mononitrobenzene is widely used as an ▮▮▮▮▮ intermediate product in the aniline dye industry for the production of aniline. A small amount thereof goes to the making of c▮▮X chlorate explosives, in which it serves as fuel and phlegmatizer.

Dinitrobenzene. Nitration of mononitrobenzene by mixed acid yields technical dinitrobenzene:

$$C_6H_5(NO_2) + HNO_3 \rightarrow C_6H_4(NO_2)_2 + H_2O.$$
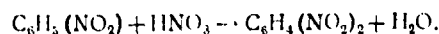
The nitration velocity of mononitrobenzene under homogeneous conditions rises, as was demonstrated by Martinsen (Bibl.84), with increase in sulfuric acid strength to 89.1%, and thereafter it falls. Hetherington and Mason (Bibl.85) have investigated this reaction under heterogeneous conditions and determined that the nitration reaction proceeds only in the mineral phase.

Mononitrobenzene may be nitrated to meta-dinitrobenzene by nitric acid in the presence of boron fluoride (Bibl.86) with a yield of up to 90%. Nitration of mononitrobenzene by sodium nitrate with excess strong sulfuric acid yields the same good yield of dinitrobenzene as when fuming nitric acid is employed.

Dinitrobenzene may be produced by XXX nitration of benzene, and in a single stage (Bibl.87).

Technical dinitrobenzene, obtained by nitration of mixed acid with f.n.a. = 86% at 75 - 80°, consists of three isomers and has the following percentage composition (Bibl.88, 89):

    Meta-dinitrobenzene . . . . 90 - 91
    Ortho-dinitrobenzene . . . . 8 - 9
    Para-dinitrobenzene . . . . 1 - 2

The freezing point of technical dinitrobenzene is 81°.

The ortho- and para-dinitrobenzene isomers constitute an undesirable impurity in meta-dinitrobenzene. The yield of the meta-dinitrobenzene isomer depends upon the nitration temperature (Bibl.88, 90) which is evident from Table 34.

Table 34

a)	b)	c)		
		d)	e)	f)
—17 to —10	86,9	95,1	2,5	2,4
—5 to +5	86,8	94,7	3,5	1,8
25—29	85,0	92,6	5,0	2,4
65—69	83,0	89,3	7,7	3,0
90—100	80,0	87,0	7,8	1,2
124—129	79,9	85,7	13,9	0,4

a) Nitration temperature °C; b) Freezing point °C; c) Percentage composition of dinitrobenzene obtained; XXXXXX d) Meta-; e) Ortho-; f) Para-

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Tables 35 - 37 present certain physical-chemical constants and properties of the isomers of dinitrobenzene, from which it follows that the meta-isomer, which is the chief product of nitration, is more soluble than the other two.

Table 35

Product	Melting Point, $^{\circ}C$	Boiling Point, $^{\circ}C$
Meta-dinitrobenzene	89,7	302
Ortho-dinitrobenzene	116,5	319
Para-dinitrobenzene	172,1	309

Table 36

a)	b)					c)
	20	90	120	140	160	
meta-	1,577	1,3644	1,3349	1,3149	1,2357	0,02528
ortho-	1,59	—	1,3119	1,2915	1,1737	—
para-	1,625	—	—	—	—	—

a) Dinitrobenzene isomers; b) Specific gravity at temperature, $^{\circ}C$; c) Viscosity at 90°, g/cm/sec

Table 37

a)	b)	c)		
		meta-	ortho-	para-
d)	20,5	6,75	3,3	0,69
e)	20,5	3,5	1,9	0,40
f)	20,0	2,4	1,09	0,30
g)	17,6	1,35	0,24	0,14
h)	17,6	32,4	27,1	1,82
i)	18,2	39,45	5,68	2,56
j)	18,2	36,27	12,96	3,56
k)	16,5	30,66	3,63	2,36
l)	16,5	1,18	0,14	0,12
m)	20,0	0,02	0,01	0,01
m)	100,0	0,32	0,30	0,30

a) Solvent; b) Temperature, $^{\circ}C$; c) Parts of dinitrobenzene dissolving in 100 parts of solvent; d) Methyl alcohol; e) Ethyl alcohol; f) Propyl alcohol; g) Carbondisulfide; h) Chloroform; i) Benzene; j) Ethyl acetate; k) Toluene; l) Carbontetrachloride; m) Water

The solubility of meta-dinitrobenzene in 100 parts of sulfuric acid XX of

various strengths is presented in Table 38 (Bibl.91).

Table 38

a)	b)		
	70	80	90
0	0,60	1,4	7,15
10	0,65	1,4	7,2
25	0,75	1,7	7,9
40	0,90	1,8	9,0
50	1,00	2,2	10,1
60	1,15	2,7	11,25
70	1,40	3,5	13,40
80	1,85	4,0	16,0
90	2,05	4,8	18,6
100	3,00	6,5	22,3

a) Temperature, °C; b) Percentage solubility of meta-dinitrobenzene

in sulfuric acid of various strengths, in %

The comparatively low solubility of meta-dinitrobenzene in sulfuric acid

facilitates the separation XX thereof from the spent acid in production.

Dinitrobenzene is a poisonous substance, and the danger of poisoning thereby

is increased by its volatility (particularly in steam).

Meta-dinitrobenzene is a neutral substance that does not react with metals.

Upon boiling with caustics, ortho- and para-dinitrobenzene form the corresponding

ortho- and para-nitrophenols. Caustic reacts with meta-dinitrobenzene only at

elevated XXXX temperature, and the reaction product XXX is apparently a complex

chemical compound of unknown composition. With sodium methylate and ethylate, the

134 ortho- and para-dinitrobenzenes form the corresponding nitro anisoles and nitro

XXXXXXX phenetoles.

Reaction of sodium methylate and ethylate with XX meta-dinitrobenzene yields

insoluble compounds, brown in color.

Ammonia and methylamine react only with the ortho- and para-dinitrobenzols,

yielding the corresponding nitroanilines and nitromethylamines, on the equation

$$C_6H_4(NO_2)_2 + CH_3NH_2 \rightarrow C_6H_4(NO_2)(NHCH_3) + HNO_2.$$
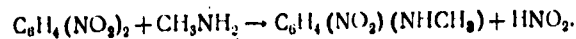
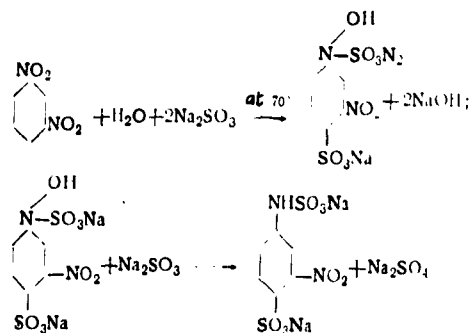Sodium sulfite exchanges a nitro group for a sulfo group in the ortho-
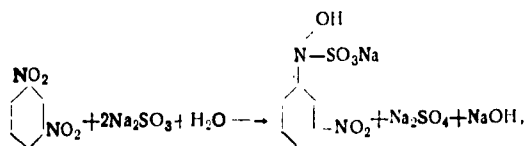
and para-dinitrobenzenes, in accordance with the equation
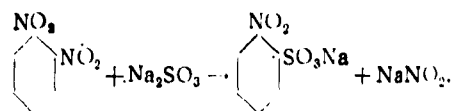
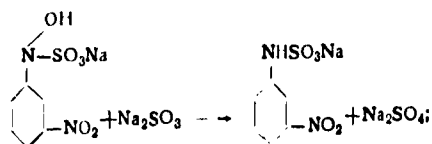Sodium sulfite reacts with meta-dinitrobenzene only at XX elevated temperature.

As was demonstrated by O.M.Golosenko, the reaction proceeds in accordance with
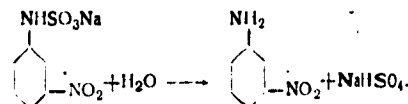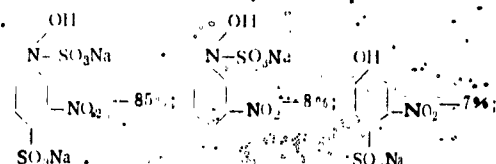
the following mechanism

There is a side reaction

which, later, upon acidification, results in the formation of unsulfated amines:
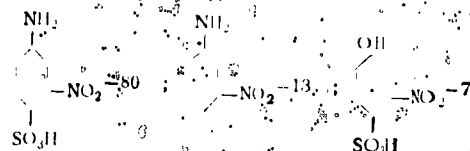
$$\text{NHSO}_3\text{Na} \qquad \text{NH}_2$$
$$\underset{\text{NO}_2}{\bigcirc} + H_2O \longrightarrow \underset{\text{NO}_2}{\bigcirc} + \text{NaHSO}_4.$$

135   The ratios between the compounds formed are:

before acidification

$$\underset{\text{SO}_3\text{Na}}{\overset{\text{OH}}{\underset{\text{N–SO}_3\text{Na}}{\bigcirc}}}_{\text{NO}_2} - 85\% ; \quad \underset{\text{SO}_3\text{Na}}{\overset{\text{OH}}{\underset{\text{N–SO}_3\text{Na}}{\bigcirc}}}_{\text{NO}_2} - 8\% ; \quad \overset{\text{OH}}{\underset{}{\bigcirc}}_{\text{NO}_2} - 7\%.$$

after acidification

$$\underset{\text{SO}_3\text{H}}{\overset{\text{NH}_2}{\bigcirc}}_{\text{NO}_2} - 80 ; \quad \underset{\text{SO}_3\text{H}}{\overset{\text{NH}_2}{\bigcirc}}_{\text{NO}_2} - 13 ; \quad \overset{\text{OH}}{\bigcirc}_{\text{NO}_2} - 7$$

Dinitrobenzene is an explosive that is highly stable at elevated temperature and of low sensitivity to mechanical influences (the shock sensitivity is less than that of TNT). Its explosive properties are about 13% weaker than those of TNT (Bibl.35).

The heat of detonation of dinitrobenzene is 820 kcal/kg, the volume of the gaseous explosion products is 635 ltr/kg, the detonation velocity 6100 m/sec, the fugacity is 255 cc, the brisance is 3.4 mm according to Kast, and 10 mm according to Hess.

Dinitrobenzene is poorly detonatable. When cast, it requires a very powerful detonator, but, unpressed, it may be detonated by a cap containing 1.5 gm mercury fulminate, whereas when pressed under a pressure of 290 kg/cm^2 and a density of 1.29 it may be detonated by a cap with 3 gm mercury fulminate, while when pressed under a pressure of 850 kg/cm^2 to a density of 1.44, it cannot be

135   detonated by a 3-gram cap.

Dinitrobenzene with a powerful detonator XX may be employed to fill shells, both as an independent explosive, in the pressed and cast condition; in each case the density of casting may be in the range of 1.48 - 1.5. Most frequently, dinitrobenzene is employed in mixtures with ammonium nitrate, as well as in the form of alloys with other explosives.

A substantial supply of raw materials for the production of dinitrobenzene is available. In this respect, it enjoys a significant advantage over the other XX individual explosives. Therefore, in wartime, the production of dinitrobenzene is expanded XXXX considerably.

A major shortcoming of dinitrobenzene is its toxicity. For this reason, it is produced in peacetime only in quantities required to satisfy the need of the aniline dye industry for XXX production of meta-nitroaniline and meta-phenylenediamine, which are intermediate products for dyes. In wartime, dinitrobenzene is frequently produced in shops that manufacture TNT (when toluene is unavailable), the starting and intermediate products employed in the manufacture of TNT and dinitrobenzene are rather XXXXXX similar in their properties.

During World War I, picric acid wax was employed in an alloy with dinitrobenzene and a little vaseline, as a phlegmatizer (87% picric acid, 10% dinitrobenzene, and 3% vaseline). In England, this alloy was used to fill armor-piercing shells, and large-caliber shells. In Germany, a mixture of potassium chlorate and dinitrobenzene of the following composition was employed: 56% $KClO_4$; 32% dinitrobenzene; and 12% dinitronaphthalene. When heated, this mixture liquifies, and it is therefore easy to fill shells with it.

136   Alloys of dinitrobenzene and TNT have not found application, as they melt at

low temperatures.

During World War II, dinitrobenzene was employed in a mixture ~~XX~~ with ammonium

nitrate and other explosives in the filling, primarily, of aviation bombs. In Germany,

aerial bombs were filled with dinitrobenzene by the so-called piece method: pieces of

PTEN, RDX, calcium nitrate, and ammonium nitrate were loaded in, ~~XX~~ and then melted

dinitrobenzene was poured in to fill up.

The use of dinitrobenzene to produce ersatz explosives makes it possible to

expand the supply of raw materials available.

Trinitrobenzene. The 1,3,5-isomer was first obtained by Hepp (Bibl.16) in

1870 by reacting very strong mixed acid with diritrobenzene at high temperature

$$C_6H_4(NO_2)_2 + HNO_3 \rightarrow C_6H_3(NO_2)_3 + H_2O.$$
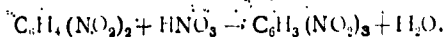
~~XXXXXXXXXXX~~

1,3,5-Trinitrobenzene is crystallized from alcohol in the form of white platelets

of rhombic shape. The freezing point is 123.25°, and the specific gravity 1.69.

The density practically attainable ~~XXXX~~ by pressing is 1.65.

Table 39 presents data on the solubility of 1,3,5-trinitrobenzene in various

solvents (Bibl.92), and Table 40 shows its solubility in sulfuric acid. The Tables

show that the best solvent for 1,3,5-trinitrobenzene is pyridine and acetone. The

solubility of 1,3,5-trinitrobenzene in sulfuric acid is practically equal to the

solubility of ~~XXXXXXXX~~ meta-dinitrobenzene (see Table 38).

Table 39

a)	b)		
	17	50	100
c)	112,60	194,23	—
d)	59,11	160,67	--
e)	29,83	52,40	---
f)	11,86	46,31	—
q)	6,18	25,70	—
h)	6,24	18,42	..
i)	3,76	7,62	—
j)	2,09	4,57	..
k)	1,70	2,72 (at 32°)	—
l)	0,24	0,44 (at 33°)	—
m)	0,03	0,10	0,50

a) Solvent; b) Solubility of trinitrobenzene (in 100 gm solvents), in gm, at temperature in °C; c) Pyridine; d) Acetone; e) Ethylacetate; f) Toluene; g) Benzene; h) Chloroform; i) Methanol; j) Ethanol; k) Ether; l) Carbonisulfide; m) Water

ТЖЖІЖ

In table 41 presents the melting point of alloys of 1,3,5-trinitrobenzene and meta-dinitrobenzene, which, as is evident from the data presented, first drops, and then increases. This testifies to the existence of a eutectic mixture of 1,3,5-trinitrobenzene and meta-dinitrobenzene. In point of fact, trinitrobenzene-1,3,5 does yield a eutectic mixture with meta-dinitrobenzene, melting at 61.9° (Bibl.87). Some investigators (Bibl.92, 93) regard this to be an unstable modification of 1,3,5-trinitrobenzene. Urbanskiy (Bibl.94) has convincingly demonstrated the absence of dimorphism in 1,3,5-trinitrobenzene.

ТЖЖІЖЖЖІЖ

Table 40

a)	b)			
	70	80	90	100
25	0,5	1,05	7,8	21,5
40	0,75	1,75	8,6	24,0
50	0,9	1,9	11,3	26,5
60	1,15	2,3	11,65	28,0
70	1,2	2,95	12,05	32,0
80	1,5	3,75	14,75	34,3
90	2,0	4,15	17,75	37,0
100	2,5	5,90	21,30	42,4

a) Temperature, °C; b) Percentage solubility of trinitrobenzene in sulfuric

acid, strength in percentage

Table 41

a)		d)
b)	c)	
100	0	120,3
90	10	109,8
80	20	98,3
70	30	86,2
60	40	74,2
55	45	65,5
50	50	61,9
40	60	65,5
30	70	72,3
20	80	78,2
10	90	84,5
0	100	89,9

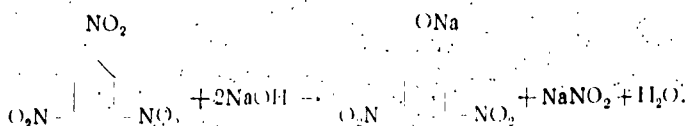a) Composition of alloy of trinitrobenzene and dinitrobenzene; %; ▨XXXXXXXX

b) 1.3,5-trinitrobenzene; c) m-dinitrobenzene; d) Melting point of alloy, °C

1,3,5-Trinitrobenzene is a neutral substance that does not react with metals

and oxides thereof. With alcohol solutions of bases, such as TNT, it yields metallic

derivatives red in color, having a low detonation point and high sensitivity to

mechanical action:

137
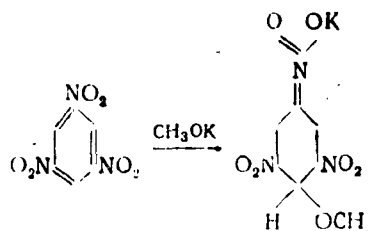
138   Reduction by tin in hydrochloric acid permits the conversion of trinitrobenzene

to triaminobenzene. Certain oxidizers (for example, $K_3[Fe(CN)_6]$) transform

1,3,5-trinitrobenzene to picric acid. The dilute solution of caustic soda converts

1,3,5-trinitrobenzene to sodium dinitrophenolates:

The effect of gaseous ammonia at low temperature XX upon 1,2,3-trinitrobenzene

leads to the formation of a reddish brown crystalline mass (with metallic glitter)

composition of which reveals a formula of $C_6H_3(NO_2)_3 \cdot 2NH_3$. The presence of

moisture , as well as reduction of temperature significantly increase the reaction

speed. Like TNT, 1,3,5-trinitrobenzene yields complexes when reacted with various

amines, as well as other compounds (Bibl.95,96). With XXX phloroglucine, in alkaline

solution 1,3,5-trinitrobenzene forms polycyclic compounds (Bibl.97).

The asymmetrical trinitrobenzenes are more reactive. Thus, substitution of

the nitro group by the hydroxyl occurs even under the influence merely of weak soda
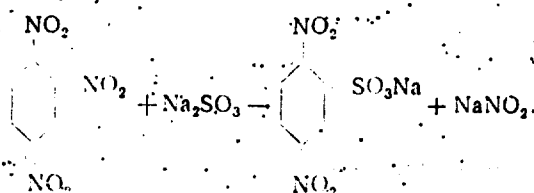
solutions:
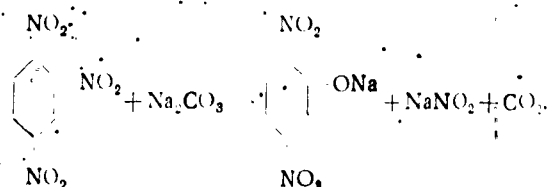
138   When asymmetrical trinitrobenzenes are heated with an aqueous ammonia solution, the nitro group is replaced by the amino group:

$$NO_2\text{-benzene-}NO_2\text{-}NO_2 + 2NH_3 \longrightarrow NH_2\text{-benzene-}NO_2\text{-}NO_2 + NH_4NO_2.$$
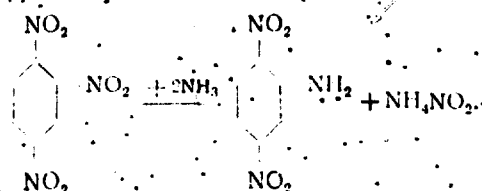
When an aqueous sodium sulfite solution is reacted with asymmetric isomers, sodium salts of dinitrobenzene sulfonic acid result:

$$NO_2\text{-benzene-}NO_2\text{-}NO_2 + Na_2SO_3 \longrightarrow SO_3Na\text{-benzene-}NO_2\text{-}NO_2 + NaNO_2.$$

Symmetrical 1,3,5-trinitrobenzene forms a compound $C_6H_3(NO_2)_3 \cdot Na_2SO_3$ in caustic or neutral solution. In acid solution this compound decomposes in with the following equation:

$$C_6H_3(NO_2)_3 \cdot Na_2SO_3 + H_2SO_4 \longrightarrow C_6H_3(NO_2)_3 + H_2O + Na_2SO_4 + SO_3.$$
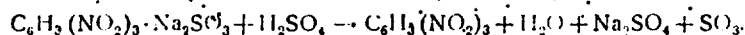
139   The method employed separates trinitrobenzene from an alloy thereof with dinitrobenzene is based upon this property.

The stability of trinitrobenzene is equal to that of TNT, whereas its shock sensitivity is considerably higher (it explodes upon the dropping of a 2 kg weight from a height of 46 cm, whereas in the case of TNT, the distance required is 100 cm) (Bibl.35). As compared with TNT, the raw materials that may be used for production are more extensive, and if a favorable solution is found to the problem of production of trinitrobenzene, it could find the same field of application as TNT. An insignificant quantity of trinitrobenzene was employed in World War I in the filling of naval armor-piercing shells.

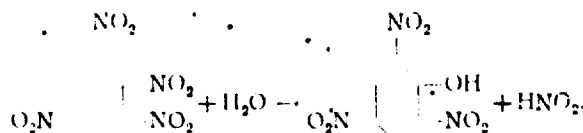Table 42 presents the explosive properties of trinitrobenzene.

Table 42

Characteristic	Trinitrobenzene
Volume of gaseous explosion products, in ltr/kg	711
Heat of explosion, kcal/kg	1104
Speed of detonation, m/sec	7300
Brisance, due to Kast, mm	4.7
Fugacity, in cc	325

. Tetranitrobenzene (Bibl.98) - the 1,2,3,5-isomer - is a crystalline, bright

yellow substance, having a melting point of 129 - 130°. It fuses without decomposition

in the fused state, and will not decompose in a 6-hour period.

The liquids containing oxygen in their molecules (alcohol, acetone, ether, etc.)

will dissolve it. In hydrocarbons and their halide derivatives, 1,2,3,5-

tetranitrobenzene dissolves to a sufficient degree (particularly when heated), and is

capable of being recrystallized therefrom.

In water, 1,2,3,5-tetranitrobenzene virtually undergoes no dissolution at all,

but when it is allowed to stand in a vessel with water, the latter acquires a yellow

coloration even within half an hour. The color is due to the reaction of 1,2,3,5-

tetranitrobenzene with water, resulting in the formation of picric acid:

$$O_2N \begin{array}{c} NO_2 \\ | \\ NO_2 \\ NO_2 \end{array} + H_2O \rightarrow O_2N \begin{array}{c} NO_2 \\ | \\ OH \\ NO_2 \end{array} + HNO_2.$$

The reaction speed increases with increase in temperature, and boiling water

completely converts 1,2,3,5-tetranitrobenzene to picric acid within a few minutes.

However, storage of the product in the air results in virtually no decomposition,

D. <u>Trinitroxylene and Other Nitro Derivatives of Xylene</u>

Trinitroxylene $C_6H(CH_3)_2(NO_2)_3$ (or xylyl) is a product of the nitration of an aromatic hydrocarbon by xylene. Trinitroxylene was first obtained in 1879 by Fittig.

As a consequence of its weak explosive properties, as well as of the comparatively (considerably less xylene than toluene is small supply of raw materials for making it ██████████████████████████████████████ found in the distillation products of coal and petroleum), ██████ xylyl has considerably less significance as an explosive than does TNT. Xylyl was widely employed in the First World War, but was used to an only insignificant degree during the ██ Second World War. During the First World War, it was produced in France, ███ the USA, and Russia.

In peacetime, xylyl is employed as a component of ammonium nitrate explosives containing 88% ████████ ammonium nitrate and 12% xylyl.

In Russia, the production of xylyl was undertaken on the initiative of prof. A.A.Solonina, who developed a method of producing it by nitration of coal light-fraction resin xylenes in mixed acid. The production of xylyl was undertaken simultaneously at three plants: the Okhta, Krotte, and Shterov. Xylyl was employed in a mixture with ammonium nitrate to fill hand grenades and mines. ██ Later, a mixture of xylyl ███ with TNT and ammonium nitrate was employed to fill shells.

Section 1. <u>Chemistry of Production, Properties, and Applications of Nitro Derivatives of Xylene</u>

Xylene $C_6H_4(CH_3)_2$ (or dimethylbenzene) exists in three ██████ isomeric forms: ortho-, meta-, and para-, in addition to which ethyl benzene $(C_6H_5C_2H_5)$ is isomeric therewith. The basic physical properties of these aromatic hydrocarbons ██ are presented in Tables 43 and 44.

Table 43

| a)	b)	c)	d)
e)	114,0	−25,0	0,881
f)	139,3	− 47,4	0,867
g).	138,5	−13,2	0,861
h)	136,2	−91,4	0,864

a) Compound; b) Boiling point, °C; c) Melting point, °C; d) Specific gravity $d_{4,0}^{20°}$;

e) Ortho-xylene; f) Meta-xylene; g) Para-xylene; h) Ethylbenzene

Table 44

Compound	Solubility in 100 gm of, at 15°		
	Water	Absolute Alcohol	Ether
Ortho-xylene	Insoluble	Soluble in any quantity	Soluble in any quantity
Meta-xylene	Insoluble	~~Soluble in any quantity~~ Sk	
Para-xylene	Insoluble		
Ethylbenzene	0.01		

When strong sulfuric acid is reacted with xylenes, the reaction with the meta-isomer goes most readily, and results in formation of meta-xylene-4-sulfonic acid and meta-xylene-2-sulfonic acid:
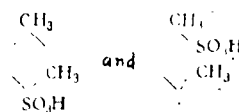
Ortho- and para-xylenes react with greater difficulty with sulfuric acid because of the difference in the effect of the methyl groups upon the orientation of the sulfo group. The reaction products are ~~XXXX~~ ortho-xylene-4-sulfonic acid and para-xylene-2-sulfonic acid (Bibl.116):
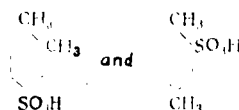
At 100°, weak nitric acid (30% HNO_3) oxidizes ortho- and para-xylene to the corresponding XXIXX toluic acids; meta-xylene does not react under these conditions.

A mixture of chromic and sulfuric acids oxidizes ortho-xylene to CO_2 and H_2O, and meta- and para-xylenes to phthalic acids (Bibl.117).

Xylene is obtained in the coking of coal and in the pyrolysis of petroleum products.

Table 45

Compound	Composition of Xylene, %	
	From Coal	From Petroleum
Meta-xylene	65—70	29—31
Para-xylene	12—15	8—11
Ortho-xylene	5—8	23—27
Ethylbenzene	8—10	21—23
Gasolines	1—2	13—15

Technical xylene consists of all three isomers and of ethyl benzene, and also contains small amounts of trimethylbenzene and gasolines. Composition of coal xylene differs sharply from the petroleum product (Table 45) (Bibl.117,118) in that it has a greater content of meta isomer and a lower content of ethyl benzene and paraffins.

Due to the small difference in their boiling points, these hydrocarbons cannot be separated by distillation.

Separation by freezing (Bibl.119) or by employment of the differences in the solubilities of the calcium salts of their sulfonic acids (Bibl.120) also does not yield XXXIXIYXXXXXXX satisfactory results. The most valuable, XX for purposes of nitration, meta-xylene, may be separated by the subjecting technical xylene to sulfonation XXX by sulfuric acid (96% H_2SO_4) at 50 - 55°. This results in the sulfonation of, and the entry into solution merely of the ortho- and meta-isomers, while the para-xylene, the ethyl benzene, and the gasolines are separated out.

The ortho- and meta-xylene sulfonic acids are decomposed by steam, the meta-xylene-sulfonic acid decomposing between 130 - 140°, and the ortho-xylene sulfonic acid

152   decomposing at 160°. The liberated hydrocarbons were driven off with the water vapor and separate from the water vapor in a condenser (Bibl.121).

Purification of technical xylene to be nitrated is unprofitable, when performed in the manner described.

Therefore, it is primarily xylene derived from coal, which contains the largest amount of meta- and para-isomers, that is chiefly employed in nitration. The content of other impurities is limited by the technical specifications, in accordance with xylene has to have a specific gravity of 0.863 ± 0.003, must go over in the 136.5 - 141.5° temperature interval, and not less than 95% of xylene must go over in a temperature range of no more than 4.5°.

Mononitroxylene. When technical xylene is nitrated by mixed sulfuric and nitric acid, technical mononitroxylene is formed.

$$C_6H_4(CH_3)_2 + HNO_3 \rightarrow C_6H_3(CH_3)_2(NO_2) + H_2O.$$
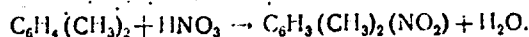
153   The nitration product is a mixture of isomers. Thus, nitration of meta-xylene results in the formation of three isomers (Bibl.122, 123), chiefly
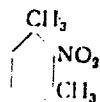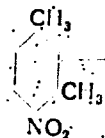
2-nitro-meta-xylene and   4-nitro-meta-xylene,

as well as a small amount of
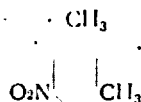
5-nitro-meta-xylene.

Nitration of para-xylene results in the formation only of

2-nitro-para-xylene

It is more difficult to nitrate ortho-xylene than the meta- and para-isomers

153   (Bibl.127), and two isomers (Bibl.128) are formed as a consequence:

CH₃
|CH₃   3-nitro-ortho-xylene and
/NO₂

CH₃
|CH₃   4-nitro-ortho-xylene
\
NO₂

Kobe and Pritchett (Bibl.129) have investigated the effects of various factors upon nitration of ortho-xylene to the mononitroderivative. They determined that, when the optimum conditions are adhered to, a yield of 90% mononitroorthoxylene may be achieved. The nitration product consists of 58% 3-nitro- and 42% 4-nitro-ortho-xylene.

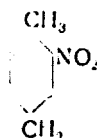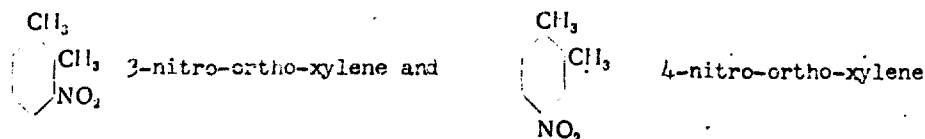Of the three xylene isomers, meta-xylene is nitrated most readily (Bibl.123, 130). Nitration of meta-xylene requires half as much sulfuric acid as does nitration of the ortho- and para-isomers.

Table 46 presents a comparison of the conditions of nitration of the isomers of xylene.

Table 46

a)	b)		e)	f)		g)	h)
	c)	d)		d)	c)		
ortho(2.2)-	6—35	25	15.8	80	78—82	60	90
para-(2.2)-	20—40	30	5.0	85	77—85	30	92
meta-(1.08)-	5—55	30	10.0	81	77—85	60	98

a) Molar ratio $\frac{xylene}{H_2SO_4}$; b) Temperature °C; c) Permissible; d) Optimal; e) Excess HNO_3, %; f) Strength of H_2SO_4, %; g) Reaction time, min; h) Maximum yield, %

Nitration of ethyl benzene forms a mixture of three isomers: ortho-, para-, and meta-. The technical product, obtained at 35 - 40°, consists of 48.5% para-, 45% ortho-, and 6.5% meta-nitro-ethylbenzenes (Bibl.131, 132).

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Para-nitroethylbenzene was recently suggested as the starting material for the production of an important pharmaceutical, synthomycin, and a continuous method of producing mono-nitroethylbenzene, with subsequent separation of para-nitro derivatives, has been developed for this purpose.

The physical properties of the various nitroxylene and nitroethylbenzene isomers are presented in Table 47.

Table 47

Chemical	Specific Gravity at 15°	Boiling Point °C	Melting Point °C	Appearance under Normal Conditions
2-Nitro-meta-xylene				Light yellow liquid
4-Nitro-meta-xylene	1.112	225	13	The same
5-Nitro-meta-Xylene	1.135	237	2	Elongated needles
2-Nitro-para-xylene	1.152	273 / 239	74 / —	Light yellow liquid
3-Nitro-ortho-xylene		240	15	The same
4-Nitro-ortho-xylene	—	228	11	Yellow prisms
Ortho-nitroethylbenzene		243 / 246	—11.5 / 37	Yellow liquid
Para-nitroethylbenzene				The same
Meta-nitroethylbenzene				The same

Dinitroxylene. When technical mononitroxylene is nitrated with mixed acid, technical dinitroxylene results:

$$C_6H_3(CH_3)_2(NO_2) + HNO_3 \longrightarrow C_6H_2(CH_3)_2(NO_2)_2 + H_2O.$$
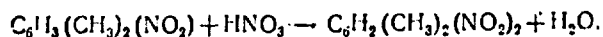
The nitration product is a mixture of isomers. Thus, 2-nitro-meta-xylene has two isomers: primarily 2,4-dinitro-meta-xylene, and a small amount of 2,5-dinitro-meta-xylene. The 4-nitro-meta-xylene isomer yields primarily 2,4-dinitro-meta-xylene; 4,6-dinitro-meta-xylene, and a small amount of 4,5-dinitro-meta-xylene. The 5-nitro-meta-xylene isomer yields 4,5-dinitro-meta-xylene.

The 2-nitro-para-xylene isomer yields primarily: 2,6-dinitro-para-xylene,

154   2,3-dinitro-para-xylene, as well as a small amount of 2,5-dinitro-para-xylene. The

3-nitro-ortho-xylene isomer yields (Bibl.128) 3,4-dinitro-ortho-xylene, 3,6-dinitro-

ortho-xylene and 3,5- or 4,6-dinitro-ortho-xylene. The 4-nitro-ortho-xylene isomer

yields 4,6-dinitro-ortho-xylene, 3,4-dinitro-ortho-xylene, and 4,5-dinitro-ortho-

xylene (Bibl.132).

For all practical purposes, the ortho- and para-nitroethylbenzenes yield only

2,4-dinitro-ethylbenzene. The meta-dinitroethylbenzene usually oxidizes as early as

the conditions obtaining in the second phase (Bibl.133).

The physical properties of the various isomers of the dinitroxylenes and XIXIXXX

dinitroethylbenzene are IIIXXXX illustrated in Table 48.

Trinitroxylene. When technical dinitroxylene is nitrated with mixed acid,

technical trinitroxylene is formed:

$$C_6H_2(CH_3)_2(NO_2)_2 + HNO_3 \rightarrow C_6H(CH_3)_2(NO_2)_3 + H_2O.$$
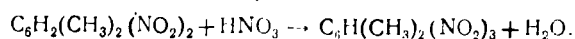
As was shown by I.I.Sidnev, the speed of this reaction under homogeneous conditions

is quite high, and does not diminish under heterogeneous conditions. This last is

explained by the fact that the trinitroxylene obtained under conditions of nitration

155   is liberated in the form of solid product and therefore does not dissolve dinitroxylene

                                                            state
(unlike TNT, which is in the liquid XXXIIXIXX under these conditions), and consequently,

does not reduce the strength thereof.

The nitration product of technical dinitroxylene is a mixture of isomers. Thus,

2,4-dinitro-meta-xylene yields two isomers: primarily 2,4,6-trinitro-meta-xylene, and·

a very small quantity of 2,4,5-trinitro-meta-xylene. The 2,5-dinitro-meta-xylene isomer

yields XXXXXXXXXXXXXXXXXXX 2,4,5-trinitro-meta-xylene. The 4,6-dinitro-meta-xylene

isomer yields primarily 2,4,6-trinitro-meta-xylene and a very small amount of

Table 48

Compound	Melting Point oC	Appearance	Solubility, gm, in 100 cc 95% Alcohol	
			at 15°	at 20°
2,4-Dinitro-meta-xylene	83	White platelets	-	-
2,5-Dinitro-meta-xylene	102	Colorless needles	-	-
4,6-Dinitro-meta-xylene	93	..	-	-
4,5-Dinitro-meta-xylene	32	-	-	-
2,-Dinitro-para-xylene	124	Thin needles	-	-
2,3-Dinitro-para-xylene	93	Monoclinic prisms	-	-
2,5-Dinitro-para-xylene	148	Yellow needles	-	-
3,4-Dinitro-ortho-xylene	82	Silky needles	-	-
3,-Dinitro-ortho-xylene	70	-	-	-
4,-Dinitro-ortho-xylene or 3,5-dinitro-ortho-xylene	70	Transparent needles	-	-
4,5-Dinitro-ortho-xylene	115	White needles	-	-
2,4-Dinitroethylbenzene	4	Oily liquid	-	-
2,4,6-Trinitro-meta-xylene	182	White crystals of rhombic form, spec. grav. 1.65	0.024	.079
2,4,5-Trinitro-meta-xylene	75	Triclinic crystal	-	1.28
4,5,6-Trinitro-meta-xylene	125	Monoclinic crystal	-	.205
2,3,-Trinitro-para-xylene	139	Yellow needles	.30	-
3,4,-Trinitro-ortho-xylene	115	Colorless needles	1.09	-
3,4,5-Trinitro-ortho-xylene	72	Yellow needles	.274	-
2,4,6-Trinitro-ethyl-benzene	37	Colorless needles	-	-

4,5,6-trinitro-meta-xylene. The 4,5-dinitro-meta-xylene isomer yields 4,5,6-trinitro-meta-xylene.

When pure meta-xylene is nitrated to the trinitro compound, it is primarily the 2,4,6-trinitro-meta-xylene isomer that is obtained, which contains only traces of the other isomers (Bibl.134).

The general yield of product is 88% of the theoretical. Nitration goes easily, and requires a 60% excess of nitric acid.

156   All three isomers of XXIXIX dinitro-para-xylene, 2,6, 2,3- and 2,5- yield 2,3,6-
or 2,3,5-trinitro-para-xylene, at 62 - 63% of the theoretical (Bibl.123, 135).

Nitration of para-xylene goes with greater difficulty than that of meta-xylene.

Upon nitration of the XX 3,4- and 3,6-dinitro-ortho-xylenes, 3,4,6-trinitro-ortho-

xylene is formed, while nitration of 4,5-dinitro-ortho-xylene results in the formation

of 3,4,5-trinitro-ortho-xylene. Nitration of 3,5- or 4,'-dinitro-ortho-xylene yields

XX 3,4,5- or 3,4,'-trinitro-ortho-xylene (Bibl.128, 135).

Ortho-xylene nitrates with considerably more XIXXISIXX difficulty than meta- and

para-xylene. Its nitration to the trinitro compound results in the production of an

oil which freezes with difficulty at 15 - 18⁰. The yield of trinitro-product is

about 54-55% of the theoretical (Bibl.135).

When ethyl benzene is nitrated to the trinitro derivative, usually, a single

isomer, 2,4,'-trinitroethylbenzene is formed. The nitration of ethyl benzene under

the same conditions as xylene IXXXXX leads to incomplete conversion to the trinitro

compound. The product contains a considerable quantity of dinitro derivative and is

an oily substance that does not solidify XXXXXXXX even at XXXX -20⁰C (Bibl.136).

The yield of this product, calculated as
trinitro compound, is 4%. It should be
noted that, due to the length of the side
chain, a considerable part of the ethyl
benzene and its nitro derivatives XX oxidize,
under conditions of nitration, to nitrobenzoic
acids (Bibl.137).

Table 49

Solvent	Solubility, gm, of 2,4,6-trinitro-meta-xylene (in 100 gm of solvent)	
	at 20⁰	at Boiling Point
Benzene	.5	7.5
Toluene	.3	21.0
Ethyl alcohol	.15	..5

The physical properties of the various trinitroxylene isomers (Bibl.138, 139) are

illustrated in Tables 48 and 49.

The quality of technical xylene is dependent, primarily, upon the composition of

the xylene being nitrated. Only the meta- and para-xylenes yield a quality non-oily

15:     product (Bibl.140). The trinitro derivatives of the meta- and para-xylenes form a

eutectic mixture of the following composition: 76% trinitro derivatives of para- and

24% trinitro derivative of meta- melting at 126° - 127°.

    Inasmuch as the technical product always contain more meta- than para-isomer, these

two isomers usually yield trinitroxylene with a melting point of 170 - 176°, corresponding

to a content of 80 to 90% of trinitro-meta-xylene, and from 20 to 10% trinitro-para-

xylene.

orthoxylene

    Mixtures of the nitro derivative of ~~orthoxylene~~ and ethyl benzene yield a liquid

oily product from which the solid trinitroxylene has to be cleansed.

    As the meta-xylene nitrates more readily than do other 6% isomers, an attempt was

made to create conditions of nitration such as to nitrate the meta-xylene to ~~mononitro~~

mononitroxylene, without nitrating the other isomers, and only then to drive off the

incompletely nitrated components from the mononitroxylene. However, work has shown

that it is not possible to nitrate meta-xylene to mononitroxylene without nitrating

the other isomers.

    In industry, technical xylene is nitrated to trinitroxylene, and only then are

the liquid oily products separated from the main product. The separated liquid oily

products are called xylene oil. The separation of the bulk of the oil from the product

is performed by treating with hot water on a centrifuge, and the residual oil is

removed by use of a solvent (extraction).

157   The technical xylyl, freed of the oil, is a fine crystalline substance, ~~fine~~ white

or slightly yellowish in color. The freezing point of the purified product is

170 - 176°, its specific gravity 1.65, its gravimetric density 0.6. Xylyl is virtually

in

insoluble in water, dissolves poorly in alcohol, and/a mixture of alcohol and benzene

298

(Table 50). Xylyl dissolves rather well in benzene and acetone.

Xylyl is a neutral substance that does not react with metal. Like TNT, xylyl

yields metallic derivatives with alcoholic bases, and these metallic derivatives have

a detonation point in the range of 142 - 165°, and a shock sensitivity less than that

of mercury fulminate, but higher than

that of lead azide. For this reason,

washing with caustics is ruled out in

the production of xylyl.

Xylyl does not form salts in

ammonium-alcohol solution, and does

Table 50

Volumetric Ratio of Solvents in Mixture		Solubility of Xylyl, %, at Various Temperatures °C	
Alcohol	Benzene	20	80
0,5	1	0,71	--
1,0	1	0,15	0,32
1,5	1	0,29	0,24
2,0	1	0,2	--

not react with gaseous ammonia (Bibl.44, 141), whereas, under these circumstances,

TNT forms compounds that are dangerous to handle. This property makes it possible to

recommend xylyl strongly for the production of ammonites. However, it must be borne

in mind that the presence of moisture, as well as conditions of low temperature,

facilitate onset of reaction between xylyl and ammonia. Caustic and carbonate bases

act upon xylyl to form metallic xylyl derivatives of greater sensitivity than xylyl.

An aqueous solution of sodium sulfite does not act upon trinitro-meta-xylene, but

does XX react with other trinitro derivatives of xylene, to form soluble sulfur salts.

The reaction follows the following equation

$$O_2N \underset{NO_2}{\overset{CH_3}{\underset{\displaystyle CH_3}{\bigcirc}}} NO_2 + Na_2SO_3 \rightarrow O_2N \underset{NO_2}{\overset{CH_3}{\underset{\displaystyle CH_3}{\bigcirc}}} \overset{CH_3}{\underset{SO_3Na}{}} + NaNO_2.$$
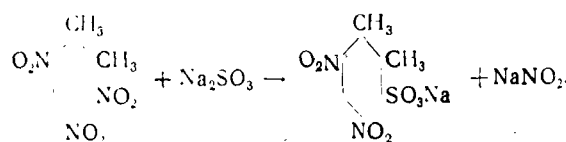
However, the purification of xylyl by an aqueous sodium sulfite solution does not,

despite the substantial losses of xylyl, yield a completely oil-free product, inasmuch

as the sodium sulfite does not react upon the nitro derivatives of ethyl benzene.

The treatment of technical XXIAX xylyl with a 5% sodium sulfite solution at 40°, for three hours, result increasing the freezing point from 162 – 163° to 168°. The treatment with a 7 – 9% sulfite solution at 70° for four hours yields a product having a freezing point of 174.°, but losses attain 24% in this process.

With respect to heating, xylyl is very highly stable and, despite the high melting point (170 – 180°), it fuses without decomposition. Its detonation point is about 330°.

When compared with TNT, xylyl is somewhat more sensitive to shock and less receptive to detonation.(the minimum initiating charge of mercury fulminate for compressed xylyl is about 0.2 gm, whereas for TNT it is 0.38 gm). Xylyl, freed of oily impurities, causes 270 cc expansion in the Trauzl block, while its brisance is 16 mm on the Hess scale, while detonation velocity is 7400 m/sec. Thus, xylyl is inferior to TNT in explosive properties.

Xylyl is employed to fill munitions in alloys with TNT, in mixtures with ammonium nitrate, and is also capable of being used in the pure form. A composition of 50% NH₄NO₃, 37.5% TNT, and 12.5% xylyl is used to fill shells, whereas one consisting of 82% NH₄NO₃ and 18% xylyl is used to fill mines and hand grenades. The mixture of 88% NH₄NO₃ and 12% xylyl is used for underground work.

Xylyl oil, which is a by-product of xylyl production, is used as a plasticizer in the manufacture of powder, and as a component of dynamite.

Section 2. Trinitroxylene Production Technology.

Xylene undergoes nitration more readily than toluene, thanks to the fact XX that it contains two metal groups, but it also oxidizes and undergoes resinification more

readily. The intensity of the oxidizing processes also increases as a consequence of

the XXXXX presence of ethyl benzene in technical xylene (the ethyl benzene is oxidized

more readily than the xylene). Xylene may be nitrated to trinitroxylene in one, two,

and three stages.

The method of nitration of xylene in a single stage, developed by A.A.Solonina,

was put into effect during World War I at three plants in Russia. Under this method,

xylene was nitrated by gradually running it into the mixed acid (79% H_2SO_4, 18% HNO_3,

and 3% H_2O) at 35°. The excess nitric acid was 45% of the theoretical. XXXX Upon
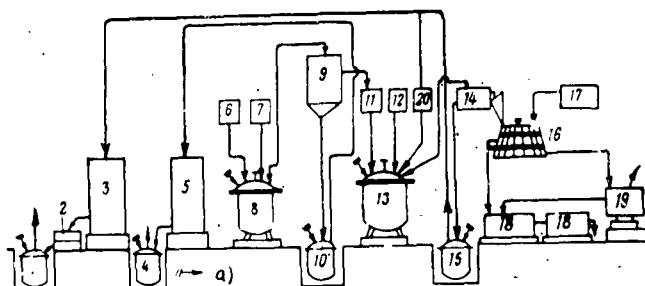
Fig.56 – Diagram of Xylyl Production

1,4,10, and 15 – Rising devices; 2,14 – Vacuum funnels; 3 and 5 – Settling columns;
6,7,11,12,17, and 20 – Measuring vats; 8 and 13 – Nitrators; 9 – Separator;
17 – Washing vat; 18 – Traps; 19 – Centrifuge

a) Compressed air

completion of run-in, it was held at 105° for an hour. The xylyl was then separated

from the spent acid on a vacuum funnel, and sent to the washing vat, where it was

washed free of acid. The washed xylyl was centrifuged and sent to drying. The

resultant product had a freezing point of 163 – 165° (Bibl.138).

A shortcoming of the single-stage method is the large yield of acids and the low

quality of the xylene. A certain advantage is the minimum need for equipment and the

simplicity of the technological process.

Another economical method is the two-stage procedure, in accordance with which, the xylene was first nitrated to mononitroxylene, whereupon the mononitroxylene was nitrated to trinitroxylene. The two-stage method was introduced into industrial practice in a somewhat modified variant.

Specifically, the first stage consists of nitration of xylene to dinitroxylene, whereas in the second, trinitroxylene is produced. Under this nitration procedure, all the spent acid is employed for the first stage, acid circulation is closed, and this reduces the acid consumed in nitration.

The three-stage method yields even greater economy of acid than does the two-stage, but the technological process is further complicated under this method (131.140).

The production of xylyl on the two-stage method is illustrated in Fig.f.

The mixed acid is poured from the measuring tank (·) into the nitrator (8), and xylene is then gradually added from the measuring tank (7). When nitration is completed, the nitro mass is forced into a separator (9), or compressed air, and separation of the fused dinitroxylene from the spent acid is performed there. After separation, the fused dinitroxylene is emitted into the measuring tank (11), and the spent acid into the rising device (10), from which it is transmitted, by compressed air, to the settling column (5). After settling, the spent acid is delivered by rising device (4) to denitration.

The second stage of nitration is run as follows. Spent acid is run into nitrator (13) from measuring tank (20), and mixed acid is run in from measuring tank (12), whereupon nitration is performed by slowly running molten dinitroxylene into the apparatus. Upon completion of the process, the nitro mass is transferred to the vacuum funnel (14), with the agitator operating. Compressed air is used to effect the

159   transfer. The spent acid is collected in rising device (15), which, as required,

functions either as a vacuum collector or as a rising device.

From rising device ~~(15A)~~ (15), the spent acid is forced partially to measuring

tank (20), the rest going to the settling column (3). After settling, the acid is

filtered through funnel (2), and sent on to rising device (1), which, like receiver (15),

functions either as a vacuum receiver, or as a rising device, depending upon necessity.

The secondary spent acid is transmitted by compressed air from rising device (1), to

the acid mixing shop to make up the first-stage mixed acid.

The xylyl, separated from the acids, is ~~transl~~ transferred to the ~~washing/the~~

washing vat (1). Washing is performed first with cold, and then with hot water, from

measuring tank (17). After each washing, the wash water is allowed to stand, and then

                                                                     to
it is poured into a system of traps (18), from which it goes ~~through~~ the sewerage

system. Upon completion of the washing, the xylyl, along with the final wash water is

drained, with agitator functioning, into centrifuge (10), where the water is separated

out, and the product is then again treated for a brief period with hot water and steam

to eliminate the bulk of xylyl oil. The xylyl oil goes to a trap along with the wash

water, and accumulates on the bottom of the trap. The xylyl, washed free of acids,

    centrifuged
and ~~drained~~ free of water, is emptied from the centrifuge into wooden boxes and is then

taken, on a ~~wagon~~ car, for final purification from oil.

The apparatus employed is standard. The cast iron nitrators have jackets, coils,

and a propeller stirrer making 160 rpm. A separator is mounted on the agitator shaft

at the level of the surface of the ~~liquid~~ liquid. The separating funnel is vertical,

has a conical bottom, and a side tap for removal of the nitro product. It is made of

iron or cast iron. The metering tank for the dinitroxylene is iron, and provided with

a coil.

                                                        a porous
        The vacuum-funnel casing is iron, and the filtering surface is ~~XXXXXX~~ ceramic

plate. Side hatches are provided in the vacuum-funnel to discharge the product. The

decanters for water washing of the product are wooden, conical vats, having a wooden

frame stirrer, and two drainage apertures: one for water (at the side wall) and one

for products (at the bottom). The capacity of the vat is 5 m^3.

        In the first stage of nitration, a mixed acid of nitric acid and secondary spent

acid is employed. Its composition is: 61 - 62% H_2SO_4; 18% HNO_3; 3% N_2O_3; 4% nitro

product and 12 - 13% H_2O. The amount of mixture for nitration is taken to provide a

10% excess of nitric acid.

        The xylene is added to the mixed acid with a gradual rise in temperature to 50°

over a two-hour period, whereupon the nitro mass is held for half an hour at 80°.

Upon completion of the process, ~~XXXXXXXX~~ the nitro product should have a specific

gravity of 1.3, and its freezing point should be in the range between 18 and 33°.

The yield is 9 - 98% of the theoretical.

        The acid mixture for the second stage has the following composition: 8% H_2SO_4

and 14% HNO_3. The quantity of mixture ~~IX~~ employed is calculated to yield a 50% excess

of HNO_3. In order to increase the module, ~~XXXXXXXX~~ spent acid is added in the amount

of 1 part by weight to 1 part by weight of dinitroxylene. The run-in of dinitroxylene

into the mixed acid is performed ~~XXXXX~~ with gradual elevation of the temperature from

70 to 80°, over a two-hour period. Then the nitro mass is held at 120° for an hour,

whereupon it is cooled to 25 - 30° at the conclusion of the process. If the mass is

sent to the vacuum filter in the uncooled state, dissolved oil, which will rapidly

     .clog
~~XXXXX~~ the pores of the filter, will separate out of the spent acid as it cools in the

pores of the ceramic plate.

The quality of xylyl is largely dependent on the manner in which the process of nitration is performed. If the conditions of nitration are violated, the resultant xylyl is in the form of very fine crystals. This complicates further processing, particularly filtering, as the pores of the filter rapidly clog. Nitration by strong acid mixtures at 50 - 75°, and holding at 120°, facilitate the formation of larger crystals. It should be noted that an increase in temperature before holding must be done very carefully, inasmuch as a rise in temperature is accompanied by a sharp increase in the oxidation of the nitro derivatives of the ortho- and para-xylenes, as well as ethyl benzene. This is accompanied by abundant separation of nitrogen oxides. The separation of the gas results in foaming of the nitrator contents. This
                          overfilling
may result in ~~overXIIIIIXX~~ of the apparatus with foam. This is combated by ~~AN~~ energetic stirring and cooling. As a consequence of oxidation of the impurities, the quality of the xylyl is somewhat impaired.

As a result of nitration, xylyl is obtained with a freezing point of about 155 - 162°. This is unsuited to military needs and ~~XXX~~ requires purification. Xylyl of this kind is a semi-solid, containing about 28 - 30% of liquid nitro derivative (nitro derivative of ortho-xylene, ethyl benzene, and the products of the lower stages of nitration of para- and meta-xylenes). The oily impurities in the xylene reduce its susceptibility to detonation. Moreover, as has been pointed out by A.G.Gorst (Bibl.138), during World War I, an oily liquid was observed to leak out of shells filled with an alloy IX of TNT and xylyl.~~XXXIXXXXXXIXXXXXXIXX~~ This impaired the physical structure of the shell.

In France, purification of the xylyl of oil was performed by washing it in five times its quantity of cold alcohol. As a consequence of the lower solubility of ~~XXIXX~~

~~XX~~

160   meta-xylene trinitro derivatives in alcohol, the meta-xylene was obtained in virtually

pure form, with a yield of about 75%. Because of the large amount of alcohol expended

(with considerable losses upon washing and recovery), this method is unprofitable.

The spent acid from stage one, and a mixture of gasoline and benzene were tried

as solvents for the oil, in the washing of xylyl. Utilization of this type of acid

renders denitration more difficult, and results in losses of liquid nitro derivatives.

Utilization of a mixture of gasoline and benzene is not very profitable. The cost

of purification rises as a consequence of the loss of solvents upon washing and recovery.

Use of these solvents is inconvenient due to toxicity and the danger of fire.

. The most practical method of removing oil from xylyl is that of washing it

with hot water on the centrifuge, where a considerable quantity of oily impurities is

removed. The xylyl going to washing contains 28 - 32 oil, and 15 - 18% after washing,

and has a freezing point of 165 - 168°. The removal of oil from xylyl washed

on the centrifuge is illustrated in the diagram in Fig.57.

Xylene is measured into extractor (1) from metering tank (2), and the xylyl is

charged in by hand, batch-wise, through the hatch, with the stirrer in operation.

Upon the completion of extraction (1 - 1.5 hrs), the mixture is allowed to stand, and

the xylene, saturated with xylyl oil, is forced into collector (4) of oily xylene, by

compressed nitrogen. After removal of the bulk of the xylene, water is run into the

161   extractor from the metering tank (3), and, with agitator operating, the entire mass is

emptied into the centrifuge (5), where the xylyl is separated from the water, and the

xylene residues. The xylyl is washed on the centrifuge with warm water to full removal

of the mother xylene (the wash water should then be transparent).

The water from the centrifuge, containing xylene, flows into receiver (6), from

306

1:1   which it goes to Florentine receiver (7), ₩₩₩₩ in which the water is separated from

the xylene. The water passes through a trap into the sewerage system, and the xylene

to receiver (8), from which it is transferred to the main collector (4).

Xylene can be completely separated from xylyl on a centrifuge, but when this is
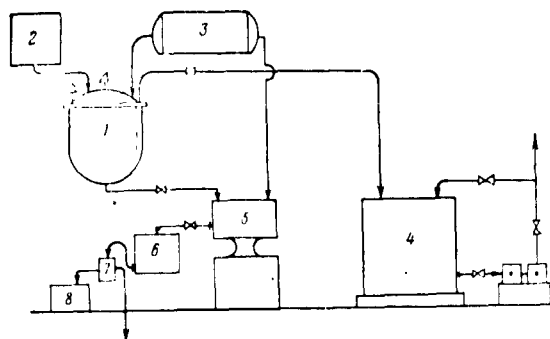
done, losses due to evaporation are great.

Fig.5" - Diagram of Purification of Xylyl

1 - Extractor; 2 and 3 - Metering tanks; 4 - Collector; 5 - Centrifuge;
- and 8 - Receivers; 7 - Florentine receiver

The xylyl freed of oil, and now containing only 2.5 - 3.5" oil, is removed for

drying in wooden boxes on cars. This product has a ₩₩₩₩₩₩₩₩₩₩ freezing point of

173 - 175°.

In extraction, 0." - 0.75 parts of xylene per weight are employed per part xylyl

by weight. As a consequence, the mother xylene obtained contains 17 - 25% oily

impurities, and a specific gravity of 0.96 - 0.98. The mother xylene is sent to

nitration. Thus, employment of the xylene as a solvent for purification of xylyl has

the advantage that the mother liquor does not require regeneration.

                                                accumulates
No more than 14 - 18% of oil ₩₩₩₩₩₩₩₩₩₩ in the xylyl going to extraction, .

because all the surplus oil is drained ₩₩₩₩ out along with the water, when the xylyl

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161   is washed on centrifuges.

The xylyl is dried for 12 hrs in a tunnel dessicator by air heated to 70 - 72°.

Before drying, the xylyl is rubbed through a No.10 sieve.

The yield of pure xylyl is 48 - 49% of the theoretical.

Xylene from petroleum XX may also be employed to produce trinitroxylene. The

                                    with the single difference that the
technological process is the same, XXXXXXXXXXXXXXXXXXXXXXXXXXXXXX amount of nitric

acid used for nitration, as well as the amount of nitro mixture is computed not on the

basis of the entire initial product, but only on the basis of the aromatic portion

thereof. The amount of excess nitric acid provided in each phase is the same as before.

In the nitration of XXXXXXXXXX petroleum xylene, certain fire danger exists because

of the presence of gasoline, particularly in the second stage, where a higher

temperature is maintained. However, thanks to the fact that the bulk of the gasolines

are removed with the XXXXXXXX fumes in the first stage, the fire danger in the second

stage is not as great.

        Xylyl
XXXXXX obtained from petroleum xylene contains considerably more oil than that

from coal xylene. In order, in part, to get rid of the oil, the spent acid from the

162   second process is diluted with XXXX spent acid from the first process, until an 83%

sulfuric acid content is attained. As this occurs, 0.11 part of oil separates out

per part of initial xylene by weight. The dilute spent acid is permitted to settle

free of the oil, whereupon the acid is removed by separation, and XXXX is then sent

in its entirety to make up the first-stage nitro mixture.

                        was
When petroleum xylene XX nitrated, the dinitroxylene was separated from the

gasolines by solution of the dinitroxylene in 98% sulfuric acid, followed by separation.

Further, the dinitroxylene, dissolved in sulfuric acid, was nitrated. The second-stage

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142 spent acid was diluted with first-stage spent acid for partial separation of the

dissolved xylyl oil, before being sent to be used in making mixed acid (for the

first stage).

E. Dinitronaphthalene and Other Nitro Derivatives of Naphthalene

The nitro derivatives of naphthalene, and particularly dinitronaphthalene

(a mixture of the 1,5 and 1,8 isomers) employed in filling shells, are considerably

less powerful than the nitro derivatives of toluene. Nevertheless, there is adequate

reason for producing dinitronaphthalene as an explosive, as this makes possible the

use of an additional source of raw material – naphthalene.

In view of its low explosive properties (detonation velocity 1150 m/sec,

expansion in Trauzl block 100 cc, compression of lead cylinder 4 mm) and its low

detonation sensitivity, dinitronaphthalene is not employed as an independent explosive.

It is widely employed as a combustible component in explosives used in military

engineering and in mining.

Thus, dinaphthalite, containing 12% dinitronaphthalene and 88% ammonium nitrate,
is
employed to fill certain types of artillery shells and mines. A mixture

consisting of 20% dinitronaphthalene and 80% TNT is employed to fill aviation bombs.

Granular dinaphthalite No.1, consisting of 12% dinitronaphthalene and 88% ammonium

nitrate, is widely employed as a moisture-resistant high explosive in underground

explosions, and no danger from gas or dust is involved. Dinaphthalite

reveals a 360 cc expansion of the Trauzl block and a brisance of 14 – 17 mm, which

permits the conclusion that it is a good ammonium nitrate explosive for resistant

rocks.

Section 1. <u>Chemistry of Production; Properties and Applications of Nitro Derivatives</u>
<u>of Naphthalene</u>

Nitronaphthalenes are produced in the nitration of naphthalene, usually as a mixture of various isomers, the number of which increases with increase in the degree of nitration. In practice, the possible maximum degree of nitration of naphthalene by mixed sulfuric and nitric acid corresponds to the production of tetranitronaphthalene. Penta- and hexa-nitronaphthalenes are produced indirectly.

The initial product is naphthalene, which is contained in relatively large quantity in coal tar (10 - 11%)*. This is particularly the case in medium and heavy oils, as well as in certain grades of petroleum, from which it is extracted by fractional distillation. The separated naphthalene is subjected to purification by caustic and sulfuric acid, with subsequent vapor distillation or volatilization.

Naphthalene is readily volatilized and sublimated. It is volatile with steam. Naphthalene crystallizes as gleaming white platelets melting at 80° and boiling at 218°. Its specific gravity at 25° is 1.1517, and at 80° - 0.9790. The latent heat of fusion is 34.39 kcal/kg.

163   Naphthalene is weakly soluble in water (0.003 gm dissolves in 100 gm of water at 25°), and is readily soluble in hot alcohol, ether, benzene, and acetone. It is readily distillable in a ~~stream~~ of steam.

The solubility of naphthalene at 16.5° in 100 gm toluene is 31.94 gm, and at 15° in 100 gm absolute alcohol it is 5.29 gm.

When naphthalene is oxidized with weak nitric acid, potassium bichromate, or potassium

---

*The yield of coal tar in the coking of Donets coals is 2 - 3% of the amount of coal charged. This tar contains up to 12.4% naphthalene (Bibl.142).

permanganate, phthalic acid is formed: $C_6H_4(COOH)_2$. With picric acid it forms the following molecular compound:

$$C_{10}H_8 + C_6H_2(NO_2)_3OH \rightarrow C_{10}H_8 \cdot C_6H_2(NO_2)_3OH,$$
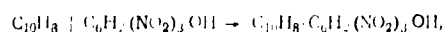
in the form of golden yellow crystals having a melting point of 149° and soluble in alcohol, ether, and benzene. Upon boiling with water, this compound decomposes. This reaction is employed for quantitative determination of naphthalene.

Naphthalene yields similar compounds with many other derivatives of the aromatic hydrocarbons, and, with each of the isomers of the di- and trinitro-derivatives, it forms a characteristic compound, different from the others. When reacted with lead tetraacetate in acetic acid solution, the naphthalene is transformed into an acetyl derivative (Bibl.143).

When hydrogen atoms are replaced by identical radicals, naphthalene is capable of yielding: two monosubstituted products (α or β), ten di-substituted, fourteen tri-substituted, and, further, twenty-two tetra-, fourteen penta- , ten hexa-, two hepta-, and one octa-isomeric derivative.

Thanks to the specific structure of naphthalene, it has a number of distinctive features, the most significant of which are the following (Bibl.144):

a) the reactivity of naphthalene is greater than that of benzene. It oxidizes, reduces, and undergoes substitution more readily, particularly in the α-position;

b) the formation of molecular compounds goes more easily with naphthalene than with benzene. This may relate to the fact that naphthalene is less saturated than benzene;

c) hydrogenation of naphthalene goes more easily than that of benzene;

d) the properties of the mono-derivatives of naphthalene differ noticeably from

163   the mono-derivatives of benzene. Moreover, the substituting group reveals a specific

influence upon the ring in which it is found, and upon the adjacent one;

e) the substitution reaction in the naphthalene ring, even in the production of

mono substitutes, is very complex: thus, the α-position is considerably more reactive

than the β-position. However, at high temperatures, when thermodynamic equilibrium

is achieved more rapidly, one will get, to cite ᵡᵡᵡᵡᵡ an example, the β naphthalene

sulfonic acid, and not the α.

Data on the heat of combustion and the formation of naphthalene and its nitro

derivatives are presented in ᵡᵡᵡ a work by Bodosche (Bibl.145), and in Appendix 18.

The following specifications must be met by naphthalene: temperature of

crystallization 79.8°, and 0.003 - 0.004 ash content. The degree of purification is

also determined by the coloration induced by sulfuric acid.

For military purposes, naphthalene is employed not only to produce nitro derivatives

therefrom, but directly as a combustible or a smoke-forming component in various

mixtures.

Naphthalene is ᵡᵡ widely employed in the production of phthalic ᵡᵡᵡᵡ anhydride,

dye synthesis, the making of plastics, etc.

Liquid products of naphthalene hydrogenation - tetralin and dekalin yield nitro

derivatives, and may consequently be used as raw materials for the production thereof.

They are also technical solvents and are, in addition to this, employed as fuels for

engines.

The production of naphthalene has ᵡᵡ reached large figures in all countries. In

the USA (Bibl.146), the discovery of a method of catalytic oxidation of raw ᵡᵡᵡᵡᵡ

naphthalene by air in phthalic anhydride has considerably increased the demand for

naphthalene. Phthalic anhydride has come into large-scale use for the production of synthetic resins, dibutyl phthalate, anthraquinone, benzoic ~~XXX~~ acid, etc. Its production ~~XXXXXXXXXXXX~~ attained 26,000 tons in 1940. In England (Bibl.147), a production of naphthalene from coal reached 80,000 tons in 1943. In Germany, more than 40,000 tons of naphthalene was produced per year in the prewar years.

Mononitronaphthalene is formed upon nitration of naphthalene with nitric acid or mixed sulfuric and nitric acids:

$$C_{10}H_8 + HNO_3 \rightarrow C_{10}H_7NO_2 + H_2O.$$
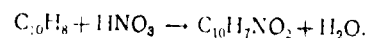
The nitration product is an α-isomer

163
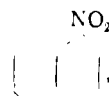
$$\text{NO}_2$$

and the oxidation products: nitrobenzoic $C_6H_4(NO_2)COOH$ and nitrophthalic
$C_6H_3(NO_2)(COOH)_2$ acids, as well as nitronaphthols $C_{10}H_5(NO_2)_2OH$.

Under certain conditions of nitration (elevated temperature and strong mixed
acid), the yield of side products increases. Thus , in technical mononitronaphthalene,
4.0 of β-nitronaphthalene and up to 3.0% 2,4-dinitro-1-naphthol was found (III 1,148).

Technical

Technical mononitronaphthalene has a freezing point of 51 - 54°. The freezing
point of β-mononitronaphthalene is 61°, and that of α- mononitronaphthalene is 72°.

α-Mononitronaphthalene crystallizes in the form of green and yellow crystals.
Its specific gravity is 1.33. It is insoluble in water, but is soluble in acid
alcohol, ether, benzene, chloroform, and acetic acid. As distinct from the di- and
trinitronaphthalenes, mononitronaphthalene dissolves readily in carbon disulfide.

The solubility of mononitronaphthalene in sulfuric and nitric acids is presented
in Table 61.

Mononitronaphthalene is readily oxidized by an acetic acid solution bichromate
in nitro-acetic acid. Weak alkaline solutions do not act upon mononitronaphthalene in
the cold, and its oxidation with formation of the oxy derivatives of naphthalene occurs
only upon heating with strong solutions.

When sodium bisulfate is reacted with α-mononitronaphthalene, the result
is 1-amino-naphthalene-4-sulfonic acid.

Studies by P.P.Shorygin and A.V.Toptov (III.149) have shown that

314

a)			b)		
c)	d)	e)	f)	d)	e)
50	41.0	0.38	50	39	0.14
50	64.5	0.75	50	58.5	0.22
50	84.0	1.12	50	70.5	0.29
60	21.5	0.36	60	37.5	0.13
60	35.0	0.72	60	55.5	0.20
70	14.0	0.28	60	66.5	0.27
70	23.0	0.42	70	21.0	0.06
70	32.0	0.56	70	32.0	0.12
80	24.0	0.81	70	46.0	0.19
—	—	—	70	53.5	0.25
—	—	—	70	58.5 .	0.31

a) Solubility in nitric acid; b) Solubility in sulfuric acid; &)XSLYSHK

c) Nitric acid strength, %; d) Temperature, °C; e) Solubility; f) Sulfuric

acid strength, %

When naphthalene is nitrated at low temperatures by excess HNO_3 (double the

theoretical), α-mononitronaphthalene is formed yielding 90 - 98% of the theoretical.

When the excess HNO_3 is great (as high as fourfold), and temperature is raised to 70°C,

1. dinitronaphthalene is formed, along with the α-mononitronaphthalene. It should be

noted that nitration under these conditions makes use only of 50% of the oxides, so

that this method is of little value, practically speaking. These authors found that

nitration of naphthalene by nitrous gases resulted in high yields of mononitronaphthalene,

even at low temperature. On the basis thereof, they proposed that naphthalene be employed

to absorb the "taillings" of gases of nitration installations, with the purpose of using

them.

Earlier studies on the nitration of naphthalene by nitrous anhydride and the

nitrosyl sulfuric acid (Bibl.150, 151, 152) were of no practical significance.

A.V.Stepanov (Bibl.153), studied the nitration of naphthalene by sodium nitrate and other nitrate salts, noted the considerable reduction in the intensity of oxidizing processes, and the improvement in the quality of the products. However, the difficulties in the recovery of the spent acids, resulting from contamination thereof by sulfate salts, renders the employment of this method for practical roles to be out of the question.

Nitration of naphthalene has been performed with XXWX weak nitric acid, accompanied by the transmission of electric current (Bibl.154). This resulted in an increase in the yield of mononitro product (45.4% instead of 23.5%).

A number of further studies on the nitration of naphthalene (Bibl.155, 156) are known. At present, they are of purely historical interest in scientific terms. We note merely the research due to Oddo (Bibl.157), to arrive at a more precise knowledge of the mechanism of nitration of XXXX naphthalene and mononitronaphthalene. He performed nitration by first treating the naphthalene with nitric acid of 1.40 specific gravity, whereupon strong sulfuric acid was added thereto at 40°. The author came to the conclusion that the oily products he obtained by nitration are complexes of nitric acid and naphthalene.

Works due to A.I.Titov (Bibl.158) demonstrated the erroneousness of QD Oddo's contention. The complex he produced proved to be a solution of nitric acid and XX mononitronaphthalene. The conclusion that SXX 1,5-dinitronaphthalene allegedly XXXXdXXXX predominated was also found to be untrue.

Fatar (Bibl.159) studied the effect of the make-up of the mixed acid, the method of introducing the reactants, and the duration of the process, upon the degree of nitration of naphthalene.

Best Available Copy

T.G.Aleksandrov and A.I.Shtam (Bibl.170) demonstrated that naphthalene would not react immediately with a mixed acid not containing nitrogen oxides. A certain time of induction is required, at the conclusion of which vigorous reaction sets in.

A.I.Titov, who observed the same phenomenon in the nitration of naphthalene by weak nitric acid (Bibl.158), holds that weak nitric acid nitrates only through the medium of nitrogen oxides, and a period of induction is required to form these. In the presence of nitrogen oxides, the reaction begins at once.

The nitration of naphthalene by nitric acid containing mercury nitrate, leads to the formation of nitronaphthols (Bibl.171).

Mononitronaphthalene is of very limited usefulness by itself.

In 1942, it was employed in Germany in smokeless low-heat powders (as 40 of the whole, replacing the derivatives of/carbamide and urethane series, which were in short supply).

Dinitronaphthalene. Technical dinitronaphthalene is usually obtained by nitration of mononitronaphthalene : mixtures of sulfuric and nitric acids, or by nitric acid. The nitration product consists chiefly of the 1,5- or α-isomer, and the 1,8- or β-isomer, with a small admixture of the 1,3- or γ-isomer
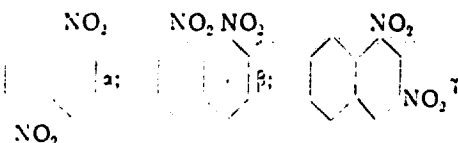
The α- and β-isomers represent 40 and 60%, respectively.

The technical product also usually contains trinitronaphthalene, mononitronaphthalene, and nitronaphthols. For example, upon nitration of mononitronaphthalene with a mixture of sulfuric and nitric acids, a product of the following percentage compositions

1,8-dinitronaphthalene 55.6

1,5- and 1,3-dinitronaphthalenes 32.6

α-nitronaphthalene 6.34

1, 4, 5- and 1, 3, 8-trinitronaphthalenes 4.23

Nitronaphthols (chiefly 2,4-) 1.2

Table 52 presents XXX certain constants of the isomer dinitronaphthalene.

Table 52

Characteristics	1,5-Dinitro-naphthalene	1,8-Dinitro-naphthalene	1,3-Dinitro-naphthalene
Melting point, °C	217	173.5	144
Shape of crystals	Yellow needles of a monoclinic system	Yellow rhombic platelets	right yellow needles

The technical product consists of hard granules, flakes or bright yellow crystals (depending upon the mode of nitration and drying) and XXXX has a melting point of 150 - 160°.

The melting points of alloys of isomeric polynitronaphthalenes, capable of being employed for thermal analysis, are presented in a work by Paskal (Bibl.143).

Table 53 presents the solubilities of α- and β-dinitronaphthalenes in certain solvents. As is evident from the Table, α-dinitronaphthalene dissolves XXXX poorly in the usual organic solvents, but better in pyridine.

Table 54 presents data on the solubility of dinitronaphthalene in nitric and sulfuric acids.

The specific gravity of technical XXXXXXXXX dinitronaphthalene at 20° is 1.50, and its gravimetric density 0.9 gm/cm^3.

Table 53

Solvent	Temperature of Solution, °C	Solubility, %	
		1,8-dinitro-naphthalene	1,5-dinitro-naphthalene
Dichloroethane	19	2.08	0.45
65% HNO₃	19	0.02	0.01
Chloroform	19	1.37	2.01
Acetone	19	6.59	0.59
Acetone	At boiling	15.98	2.3
Benzene	19	2.01	0.5
Benzene	At boiling	7.44	3.88
Ethyl alcohol (95°)	19	0.04	0.04
Acetic acid	At boiling	2.01	0.43
Carbondisulfide	At boiling	–	insoluble
Absolute ethyl alcohol	22	0.37	0.14
Gasoline	50	0.04	0.02
Water	At boiling	0.07	insoluble
Pyridine	20	–	0.8
Pyridine	At boiling	–	9.1

Upon slow heating to 318°, dinitronaphthalene decomposes with formation of foam. Ignition by a heated wire occurs at 245°.

In strong sulfuric acid, dinitronaphthalene becomes dark due to the formation of naphthazarine (5,8-dioxi-α-naphthaquinone). Formation of this product may take place via the isonitroso compound of nitronaphthoquinone:
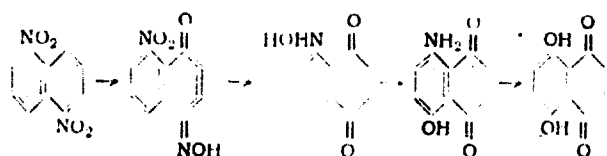
These reactions go very slowly with sulfuric acid, but considerably more rapidly in

Table 54

a)	b)				c)
	60	70	80	90	
15,5	—	0,09	0,82	--	—
25,5	0,07	0,14	1,00	13,1	0,05
31,5	—	0,21	1,87	15,05	—
42	—	0,35	—	—	--
48	0,14	0,42	—	—	0,22
55	0,23	0,49	—	—	—
61,5	0,29	0,59	—	—	—
67,5	0,44	...	—	—	--

a) Temperature, °C; b) Solubility of dinitronaphthalene in %, in nitric acid of various strength, %; c) Percent solubility in 90% H_2SO_4

in the presence of nitric acid. For example, when trinitronaphthalene is subjected to the reaction with mixed acid having a high factor of nitrating activity, the consequence is a product having the lower nitrogen content than the initial dinitronaphthalene.

Reaction of nitric acid and zinc with 1,5-dinitronapthalene at 110° results in the formation of a-nitronaphthoquinone.

At 150°, the dilute nitric acid oxidizes 1,5-dinitronaphthalene into the nitro derivatives of phthalic and benzoic acids. Reaction of sodium bisulfite yields 1,5-diaminonaphthalene-sulfonic acid
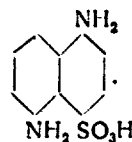
Sodium sulfite and caustic alkalies have no noticeable effect upon 1,5-dinitronapthalene.

1,8-dinitronapthalene reacts with sodium sulfite. Its behavior toward acids and

bases is the same as that of 1,5-dinitronaphthalene. 1,3-Dinitronaphthalene reacts with sodium sulfite, but less strongly than does 1,8-dinitronaphthalene. 1,3-Dinitronaphthalene is readily soluble in alcohol. Upon heating, it volatilizes (Bibl.164).

2,4-Dinitronaphthalene may be prepared from 2,4-dinitro-para-toluenesulfono-1-naphthalide without isolation of the intermediate amine (Bibl.165).

1,6-Dinitronaphthalene has been obtained from para-sulfonotoluene-2-naphthylamine dissolving it (50 gm) in hot concentrated acetic acid, and subsequent treatment of the acetic acid (specific gravity 1.42) at 55° (Bibl.166). The resultant product was subjected to diazotization in sulfuric acid. Then, the diazo compound was converted

naphthalene

to the 1,6-dinitronaphthalene by heating in alcohol solution.

1,6- and 1,7-Dinitronaphthalene are produced by nitrating β-mononitronaphthalene with mixed acid (Bibl.167).

4,5-Dinitronaphthalene [identical to 1,8-dinitronaphthalene (Bibl.168)] was obtained in the following way: α-naphthaldehyde was converted, with malonic and acetic acid, to α-naphthylmalonic acid, which converted to naphthylacrylic acid. Nitration of the latter, followed by oxidation, yielded, 4,5- or 1,8-dinitronaphthalene.

Nitration of α-mononitronaphthalene by a mixture of nitrosyl sulfuric and nitric acids (solution of SO_2 and HNO_3, specific gravity 1.50) at 20° was performed in a carbontetrachloride medium (in different solvent), as a consequence of which a mixture of 1,3- and 1,5-dinitronaphthalene was obtained (Bibl.169).

Nitration of naphthalene by fuming nitric acid or by mixed acid leads to the formation of dinitronaphthalene (Bibl.170), consisting of a mixture of the 1,5- and 1,8

Dinitronaphthalene is an explosive comparable in strength to dinitrotoluene,

but somewhat weaker than the latter (Bibl.171). Its detonation point is 300-310°,

its detonation velocity 1150 m/sec (at a density of 1) (Bibl.172), expansion in the

Trauzl block is 100 cc, Hess brisance is $\cancel{\text{XXX}}$ 4 mm at density 0.9, with a detonating

cap No.8.

As a consequence of the weak explosive properties and the low sensitivity to

detonation, dinitronaphthalene is not employed by itself as an explosive. It enters

into the make-up of explosives employed in military engineering and in mining.

A number of formulas containing dinitronaphthalene have been developed and

adapted for filling of munitions. A mixture of 48.5% dinitronaphthalene and 51.5%

picric acid, called the "Russian mixture", was widely employed during World War I to

fill artillery shells of small and medium caliber, and aerial $\cancel{\text{XXXX}}$ bombs. In France,

a formula consisting of 20 dinitronaphthalene and 80% picric acid was developed, and it

$\cancel{\text{XXXXXXXX}}$ came to be known as the "French mixture" (melting point 104°). This mixture

was used in France and a number of other countries to fill artillery shells, aerial

                                                                    advantages
bombs, and hand grenades. The "Russian mixture" had some $\cancel{\text{XXXXXXXXXX}}$ for filling

purposes because its melting point was 82 - 87°.

Dinitronaphthalene began to be used for military purposes, in mixtures with ammonium

nitrate, starting in 1909. $\cancel{\text{XXXXXXX}}$ Mixtures consisting of 88% NH_4NO_3 with 12% $\cancel{\text{XXXX}}$

dinitronaphthalene, and 80 NH_4NO_3 with 20% dinitronaphthalene, and given the designation

$\cancel{\text{XXXXX}}$ dinaphthalites (schneiderites) are employed to this day.

In 188%, Favier developed a mixture of 88% NH_4NO_3 and 12% dinitronaphthalene for

underground explosive work, as a safer explosive than dynamite.

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Explosives containing various quantities of dinitronaphthalene came into use in all countries.

In the Soviet Union, the following dinaphthalites came into use, starting in 1935, for underground work in mines not dangerous in terms of gas and dust: granular No.1, and pressed No.2, containing 12% and 8.5% dinitronaphthalene respectively.

As a consequence of treatment on crusher rolls, the brisance of granular dinaphthalites is considerably higher than that of the Favier formula (when prepared in the usual manner, the Favier formula has 9 mm brisance and 265 cc fugacity, whereas after treatment on the crusher roll, it has a brisance of 14 - 17 mm and a fugacity of 320 - 340 cc).

Dinaphthalite is one of the powerful ammonium nitrate explosives employed to blast resistant rock. Moreover, of all the ersatz high explosives of the ammonite type, only dinaphthalite satisfies the requirement in terms of emission of toxic gases (50 ltr toxic gas per 1 kg high explosive). This important indicator is of major significance in explosive undertakings in closed spaces.

Granular dinaphthalite has a brisance of 15 mm, a fugacity of 320 cc, and is subject to detonation between two cartridges at a distance of 5 mm. The grain size has a major influence upon brisance. The formula having minimum particle size provides greatest brisance and susceptibility to detonation.

When dinaphthalite is treated on roll crushers, the result is a dense mixture of dinitronaphthalene and NH_4NO_3, which also makes for a certain stability to water. This quality makes it possible to employ dinaphthalite in wet face lining.

In France, dinitronaphthalene is employed in ballistic powders.

Dinitronaphthalene is employed in the aniline dye industry as an intermediate for producing granular brown dye. It is observed that, with increase in the 1,5-dinitronaphthalene isomer, the coloration becomes more stable and of better tint.

Moreover, with increase in the 1,5-isomer, a higher yield of dye is achieved.

1,8-Dinitronaphthalene is employed to produce 1,8-naphthylenediamine, which is employed (in the form of its acetyl derivative) in the production of azo dyes.

Trinitronaphthalene. Nitration of 1,5-dinitronaphthalene yields a mixture of the following compositions (in %):

    1,2,5-trinitronaphthalene 47.5
    1,3,8-trinitronaphthalene 24.0
    1,4,5-trinitronaphthalene 9.0

(the residue consisting of impurities).

Upon nitration of 1,8-dinitronaphthalene, a mixture of the following composition (in %) is obtained:

    1,3,8-trinitronaphthalene 85.1
    1,4,8-(identical to 1,3,8- and 1,4,5)-trinitronaphthalene . 9.5

(the residue consisting of impurities).

Technical trinitronaphthalene is of the following percentage compositions (Fig. 179):

    α (1, 3, 5)-trinitronaphthalene 13
    β (1, 3, 8)-trinitronaphthalene 56
    γ (1, 4, 5)-trinitronaphthalene 8
    δ (1, 2, 5)-trinitronaphthalene 23

The isomeric position of technical trinitronaphthalene varies within certain limits in accordance with the conditions of nitration and, correspondingly,

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the melting point fluctuates in the range of 110 - 160°. Under given conditions, a mixture of tri- and tetra-nitronaphthalenes is obtained (Bibl.174).

1, 3, 5-Trinitronaphthalene was obtained by Aquiar (Bibl.170) by nitration of 1,3-dinitronaphthalene. 1,3,5-Trinitronaphthalene forms monoclinic crystals melting at 123°, and soluble in acetic acid, chloroform, and alcohol.

1,3,8-Trinitronaphthalene is obtained upon nitration of 1,8-dinitronaphthalene, and crystallizes in the monoclinic form. The melting point is 218°; it is soluble in alcohol, and weakly soluble in ether and chloroform.

1,4,5-Trinitronaphthalene crystallizes in the form of glittering yellow platelets melting at 147°. It dissolves readily in benzene AWKAKA and weakly in ether, alcohol, and chloroform.

1,2,3-Trinitronaphthalene crystallizes in the form of a needle melting at 112 - 113°, and readily soluble in alcohol.

When caustics are reacted with technical trinitronaphthalene, the latter goes into solution weakly, giving the caustic a dark red coloration. An aqueous solution of sodium bisulfite I dissolves trinitronaphthalene in the cold, while upon heating, it converts it to the corresponding nitroaminonaphthalenesulfonic acid.

Sodium sulfite reacts with all isomers of trinitronaphthalene.

At a high temperatures, strong sulfuric acid reacts with trinitronaphthalene, converting it into the solution of dark brown or black color.

In its explosive properties, this product is similar to dinitrobenzene. Table 55 adduces the explosive properties of trinitronaphthalene in mixtures with ammonium nitrate and with other nitro compounds. Upon explosion, trinitronaphthalene liberates 414 ltr/kg of gaseous products, while the heat of explosion is 923 kcal/kg.

Medard showed that the detonation of velocity of trinitronaphthalene may, under

certain specific circumstances, exceed 4400 m/sec, and that dinitronaphthalene does

not display stable detonation (Bibl.172).

Table 55

| a) | b) | c) | d) | | g) | h) |
			e)	f)		
	\	307	3,24	---	—	1,52
j)	12	228	2,16	—	5640	1,43
k)	18	106	3,95	7,6	—	1,6 0,74
l)	21	374	—	7,5	—	0,74 Hess' test
m)	4	285	3,11		—	1,55
n)	12	301	3,28			1,55
o)	12	299	3,39	—	—	1,62
p)	12	312	3,72	---	—	1,63

a) Formula; b) Shock sensitivity (weight 10 kg, h = 25 cm), in 5 explosions;

c) Trauzl fugacity (TNT No.8 cap), cc; d) Brisance (No.8 cap), mm; e) Kast; f) Hess;

g) Detonation velocity, m/sec; h) Filling density, gm/cm^3; i) TNT; j) Technical
trinitronaphthalene (melting point 150°); k) 16.3% trinitronaphthalene and 83,7% NH$_4$NO$_3$;
l) 33.6% trinitronaphthalene and 66,4% NH$_4$NO$_3$; m) 35% trinitronaphthalene and 65% TNT
(freezing point 75°); n) 15% trinitronaphthalene and 85% TNT (freezing point 74°);
o) 40% trinitronaphthalene and 60% trinitrophenol (freezing point 82°); p) 20%
trinitronaphthalene and 80% trinitrophenol (freezing point 105°)

Table 55 shows that in its fugacity trinitronaphthalene is weaker than TNT ;

20o– 25°, in brisance by 25 - 30%, but that its shock sensitivity is XX higher than

that of TNT.

not produced in significant
Trinitronaphthalene is XXXXXXXXXXXXXXXXXXXXXXXXXXXX quantity anywhere. It

was employed in Germany as a partial substitute for TNT in the form of an alloy

consisting of 47% TNT and 33% trinitronaphthalene, for the filling of shells. Small

quantities were employed in France in a mixture of 95% NH₄NO₃ and 5% trinitronaphthalene,

for the manufacture of safety explosives. IX

Tetranitronaphthalene. According to A.G.Gorst (Bibl.175), the nitration of

1,8-dinitronaphthalene yields chiefly 1,3,6,8-tetranitronaphthalene, or the β-isomer.

Its melting point is 202°. When 1,5-dinitronaphthalene is nitrated, the result consists

primarily of two isomers of tetranitronaphthalene: 1,2,5,8- or the δ-isomer, which,

upon heating at 270°, decomposes, and the 1,3,5,8-, or γ-isomer, the melting point of

which is 194 - 195°. Further, the 1,4,5,8-isomer was also obtained. It decomposes at

a temperature of about 300°, without previously having fused. Finally there is the

σ -isomer the position of the nitro groups in which has not been determined. When it is

crystallized out of chloroform, the result is crystals of rhombic form with a melting

point of 259°.

When technical trinitronaphthalene is nitrated to tetranitronaphthalene with mixed

sulfuric and nitric acids, 110 kcal heat is emitted for every 1 kg of trinitronaphthalene.

tetranitronaphthalenes are obtained
Davis points out (Bibl.177) that XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX upon the

nitration of dinitronaphthalene in the the presence of H₂SO₄ at a temperature of 80°,

and an adequate excess of nitric acid.   The product yield does not exceed 50%.

Technical tetranitronaphthalene consists of four isomers, and is readily soluble

in acetic acid. The acid equilibrium of tetranitronaphthalene somewhat exceeds that of

171   TNT, and therefore, the pure product should not be inferior to TNT in its explosive

properties.

Tetranitronaphthalene is not produced anywhere on an industrial scale because of

its high cost (large acid consumption).

Nitration of sulfo derivatives of naphthalene. Nitration of the sulfo derivatives

of naphthalene does not result in the forcing out (substitution) of the sulfo group by

nitro groups as occurs, for example, in the nitration of sulfophenols. In the case of

the sulfo derivatives of naphthalene, the nitro groups enter the ring in the meta position

with respect to the sulfo groups XX already present, when nitration occurs.

Lantz
ØⱮαꙆꙆ (Bibl.178) studied the conditions of nitration of mono-, di- and

trisulfonic acids of naphthalene in sulfuric acid solution and found that the most

favorable results are obtained when a mixture containing 85 - 90% sulfuric acid is

employed. Under optimum conditions of nitration, a maximum of four groups may be

introduced into the naphthalene ring (counting the SO_3H already present, and the NO_2

groups entering).

Here it is important to note XXXX the fact that the corresponding nitro derivatives

of naphthalene cannot be obtained from the naphthalene sulfonic acids in solution, and

therefore conveniently in the technological sense. However, in the production of XXXXXX

nitrosulfonic acids, it is desirable first to perform sulfonation, followed by nitration.

The performance of nitration immediately after sulfonation makes it possible to employ

sulfuric acid in the sulfo batch. Moreover, if the processes were run in reverse order,

sulfonation of nitro compounds might result in a small yield of the required compound

and in contamination thereof with side products, as a consequence of the ability of

nitronaphthalenes to react with strong sulfuric acid.

In the products obtained upon nitration of naphthalene, F.F.Beilstein and

A.A.Kurbatow (Bibl.156) discovered phthalic, ~~XXX~~ nitrophthalic and nitrobenzoic acids,

~~XXXXXX~~ nitronaphthols, etc.

With increase in the strength of the mixed acids and the nitration temperature,

there is an increase in the intensity of the oxidizing processes, particularly those

pro~~eding~~ with destruction of one benzene ring of the naphthalene.

~~XXXXXXXXXX~~
Section 2. <u>Technology of Nitronaphthalene Production</u>

Production of mononitronaphthalene. Mononitronaphthalene is produced by nitration

of naphthalene with mixed sulfuric and nitric acid of various compositions, having an

identical factor of nitrating activity ($\cdot 1 - \cdot 2$" in terms of H_2SO_4). Before nitration,

the naphthalene is pulverized (or fused) and first mixed with spent acid from the

preceding operation. The run-in time is employed to regulate the rate of heat emission,

so as to hold the temperature at $50 - \cdot 0^o$. At the end of run-in, the product is held

for 3 hr. The product is separated from the spent acid in the fused state. The

product should have a freezing point of not less than 51°, and its yield is $97 - 98\%$
~~XXXXXXXXXXXXXXXXXXXXX~~
of theoretical. In some cases, the production of technical mononitronaphthalene for

the needs of the aniline dye industry ~~XXXXXX~~ special conditions of nitration are

developed and a special purification of the product is performed.

Production of dinitronaphthalene. A number of industrial methods of producing

dinitronaphthalene are known. ~~XXXXXXXXXXX~~

According to Shtettbakher (Bibl.179), it is recommended first that one part

mononitronaphthalene be mixed in the nitrator with four parts commercial sulfuric

171   acid of XXX 1.84 specific gravity, whereupon 0.8 of nitro mixture is slowly poured into
the contents. The nitro mixture is prepared of equal quantities of strong sulfuric
and nitric acids. The dinitronaphthalene, that comes into being in the form of yellow
crystals, is separated from the acid on the centrifuge, and is washed with hot water XX
until a neutral
XXXXXXXXXXXXXXXXX reaction is obtained. In the given case, nitration is performed
in excess strong acid, which can be utilized only in part, in the first phase of nitration.

172   . According to the data of A.A.Scloninia (Bibl.180), Germany had a method of
producing dinitronaphthalene by nitration of mononitronaphthalene with strong nitric
acid in the cold. Detailed technical information with respect to this method is now
available. According to his data (Bi 1.180), dinitronaphthalene was made in Germany
during World War I by mixing 18 kg mononitronaphthalene and 39 kg sulfuric acid of
1.84 specific gravity, subsequent to which 15 kg strong nitric acid was run in.   In
     course of the
the/reaction process, which lasted for 8 hrs, the batch was periodically agitated.
The resultant product was filtered and washed with water. This method is not economical,
as it is based on a considerable excess of nitric acid (more than 200%) over the
theoretical.

A more profitable process was organized at a plant of the Franco-Russian Society
in Shterovka in 1914 - 1915. A mixture of 58% H_2SO_4, 28 - 30% HNO_3, and 22 - 23% H_2O,
with a 70% factor of nitrating activity, was employed to produce dinitronaphthalene.
Nitration of mononitronaphthalene was performed over a four hour period at 48 - 50°.
Twelve parts mononitronaphthalene were run into 44 parts of mixture. After 30 min of
holding of the mass in the apparatus, it was cooled to 25 - 30°, and made over for
filtration. The product removed from the acids was washed with water in 5% soda solution,

XXX   330

172   and again in cold water, subsequent to which it was washed on the centrifuge and dried

at 60 - 70° in a rack dessicator.   The spent acid was employed in the first stage of
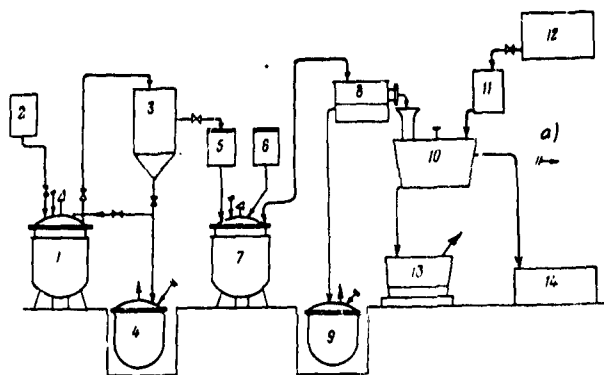
nitration.

Fig.58 - Method of Producing Dinitronaphthalene

1 and 7 - Nitrators; 2, 5, 6 and 11 - Metering tanks; 3 - Separator;
                                            (Suction Filters);
4 and 9 - Rising devices; 8 and 13 - Nutsches; 10 - Washing vat;

12 - Heater; 14 - Trap

a) Compressed air

During World War II, dinitronaphthalene was used in a single stage in Germany

(Fig.181) by nitration of naphthalene with mixed acid of the following composition:

58.5% H_2SO_4; 22.2% HNO_3; 19.3% H_2O.   The components were run-in in "inverse" water.

The temperature at the time of mixing was held at $34 - 38°$, while that at the end

of the process was 40 - 50°. Upon completion, the mass was cooled to 30°, and sent

on to a filter. Washing was performed first with cold water ($6 m^3$ per ton dinitronaphthalene), and then

with hot water ($12 - 14 m^3$). Drying was performed at 70 - 80°. The yield of dry

products 80% of the theoretical.

The production of dinitronaphthalene in two phases, by a batch process, employing

mixed sulfuric and nitric acids as a nitrating agent, is illustrated in the diagram

in Fig.58. .

     According to the diagram, naphthalene is charged into the nitrator (**1**), where a

certain amount of spent acid from the first stage ~~KKK~~ has been left as medium. Run-in is

through the hatch, with the agitator operating. Then, nitro mixture is gradually

run-in from measuring tank (2), and the nitro mass is held ~~KKö~~ for some time, to

permit stirring. Upon completion of the process, the stirrer is stopped, and the

nitro mass is permitted to stand, whereupon a portion thereof is forced into

separator (3) by compressed air.~~öf~~

The entire mononitronaphthalene is forced out of the nitrator. A portion of the

spent acid is left in the nitrator, where it serves as medium in which to perform the

following operation.

     The product tube for ~~AKII~~ delivery of acid and the products into the separator

does not reach the bottom of the nitrator. This makes for ~~the~~ maintenance of a constant

residue of spent acid in the nitrator for the ~~XKKKXKKXKKXKKXKKXIKKX~~ next first-stage operation.

     From separator (3), the mononitronaphthalene that has settled out is sent to

metering tank (5) for the second phase, and the spent acid is sent to a settling tank

through ~~rising device~~ the riser (4).

     All the nitro mixture to be nitrated is run from measuring tank (6) to nitrator (7),

whereupon, the molten mononitronaphthalene is slowly run in, with the agitator

operating.

     Upon conclusion of the run-in and holding of the nitrator contents, with the agitator

operating it is then sent to the Nutsch (8), with the aid of compressed air. Here the spent acid is squeezed out of the dinitronaphthalene. The spent acid is sent to settling columns via rising device (9), and the product is raked into the funnel through the side hatch in the Nutsch by X means of special rakes. From here it goes, via a wide pipe, to the washing vat (10).

The dinitronaphthalene obtained is washed several times with hot water. The wash water is then sent, by means of an overhead pipe, to a system of traps (14), and then to the drainage system. The hot water for washing comes from heater (12) through metering tank (11). Upon completion of washing, the dinitronaphthalene and the water are lowered over a Nutsch (13), with agitator operating, where the product is squeezed free of water. The pressed dinitronaphthalene is loaded into special cars and sent to drying along a narrow-track railway.

It should be noted that the yield of products both in the first and the second stage are dependent, to a considerable degree, upon the property of the naphthalene employed. The use of pressed naphthalene instead of crystalline naphthalene (which is pure) results in a reduction in the yield in stage one by approximately 5% and in stage two by approximately 3%.

In stage two, the mixture consisting of 44% H_2SO_4 and 15% HNO_3 is employed. The higher percentage of nitric acid facilitates the lumping of the nitro products in the course of nitration. The amount of nitro mixture is determined on the basis of assuring a 40% excess of nitric acid monohydrate over the theoretical. Complete separation of the spent acid from the dinitronaphthalene does not prove possible, and up to 30% goes to the washing vat, along with the dinitronaphthalene.

The spent acid from stage two is employed to make up mixed acid for stage one,

the factor of nitrating activity of which should be $61 - 62\%$. The composition of the

mixed acid of stage one will vary. For example, a mixture of 45% H_2SO_4, 37% HNO_3, and

18% H_2O will be used, and if the second-stage spent acid and weak nitric acid are

completely employed in stage one, the consequence is a mixture containing from

$10 - 13\%$ HNO_3 and $56 - 57\%$ H_2SO_4, with a factor of nitrating activity of $61 - 62\%$.

Nitration is performed in stage one with a gradual rise in temperature to 50°

toward the end of run-in of nitro mixture, and with holding at 60° for 1 hr. In the

second stage, nitration is performed by running the ~~MONONITOLUENE~~ mononitrotoluene

into the mixed acid over a period of 4 hrs, with gradual rise in temperature from

$15 - 18^o$ to 40°. This low temperature is required during the run-in time, as a

consequence of the tendency of the nitro product to lump at higher temperatures.

The mononitronaphthalene entering a cold, energetically agitated nitro mixture

freezes in the form of fine granules. Gradually, starting at the surface, the granules

of mononitronaphthalene undergo nitration in depth. The process of nitration proceeds

in the solid phase, and its velocity is ~~XXXX~~ determined by the rate of diffusion of

acid mixture within these granules.

It is particularly important, in the nitration process, to ~~XXXXXXX~~ adhere to the

temperature conditions, as the lumping of the product depends upon this. Because of

lumping it is the formation of a ~~XXXXX~~ low-melting mixture at a given ratio between

dinitronaphthalene and mononitronaphthalene (40 and 60% respectively).

Table 54 presents the freezing points of alloys of dinitronaphthalene and

~~XXXXXXXXXXXXXXX~~ mononitronaphthalene. Upon achievement of a formula approximating or

174 equalling the eutectic, the granules of products will begin, if temperature is elevated, to soften and merge. into lumps. Table 56 shows that the melting point of a eutectic mixture of ~~XXIXX~~ pure dry mononitronaphthalene and dinitronaphthalene is 43.5°, and that of the product impregnated with acid is even lower.

Table 56

a)		d)	a)		d)
b)	c)		b)	c)	
0	100	157,3	60	10	43,5
5	95	152,8	80	20	44,4
10	90	148,8	85	15	46,6
15	85	145,2	90	10	48
40	60	123,8	95	5	50,1
50	50	112,5	100	0	53

a) Alloy composition, %; b) Mononitronaphthalene; c) Dinitronaphthalene;

d) Freezing point, °C

In practice, there are cases in which the entire product ~~XX~~ merges into a single viscous mass that adheres to the agitator and the walls of the nitrator. Even ~~XXX~~ a small amount of lumping, leading merely to a little increase in grain size, sharply increases the nitration time and complicates further processing of such a product. The use of mixed acids for the second phase having a nitric acid content of more than 15% makes for lumping of the product inasmuch as nitric acid substantially diminishes the ~~XXXXXXXXX~~ melting point of a eutectic mixture.

Thus, running mononitronaphthalene into mixed acid is terminated at 40°, subsequent to which the temperature is raised to 45°, and the mass is held at this temperature for 1.5 hr.

After the spent acid is separated out, the dinitronaphthalene is washed repeatedly,

335

174   first with cold, and then with hot water. As a consequence of the fact that nitration

results in producing dinitronaphthalene in the form of granules, washing presents

serious difficulties. The acid trapped inside the hard granules can only be washed

out with great difficulty and it usually takes 10 or 12 washings to reduce the

acidity of the product to 0.1%. In addition to a considerable lengthening of the time

~~XXXXXXXXXXXXXXX~~ required for the process of washing, a considerable quantity of waste

waters requiring special ~~XXX~~ cleaning. ~~results.~~ ~~XXXXXXXXXXXXXXXXXXXX~~

The washed product is dried by two methods: in chamber driers on racks at 90 - 95°,

or, in the same manner as TNT, in the fused condition, at 160 - 180°, in drying baths.

Drying is followed by flaking. In this situation, the product is produced in the form

of fine flakes.

Production of trinitronaphthalene. A number of investigators have concerned ~~XXXXXXXX~~

~~XXXX~~ themselves with the manufacture of trinitronaphthalene.

175   Patard (Bibl.159) has nitrated naphthalene with mixed acids of various compositions

at 110°. He has found groups of nitro mixtures of various compositions capable of

nitrating naphthalene to specific degrees of nitration. A.V.Sapozhnikov (Bibl.176),

who elaborated on Patard's material, showed that trinitration of naphthalene can be

carried out by mixed acids containing not more than 50 molar and not less than ~~XXXXXXXXXXXXXXXXXXXXXXXXXXX~~

25 molar percent H_2O. When the mixed acids are stronger than this, the result is, at

first, tetranitronaphthalene at up to 20% molar H_2O, followed by the possibility of

partial carbonization.

Friendler (Bibl.182) produced trinitronaphthalene by direct nitration of

mononitronaphthalene.

A.A.Solonina (Bibl.180) provides a recipe for producing trinitronaphthalene,

336

employed at the Okhta Powder Works, under which 11 kg mononitronaphthalenes are mixed

with 39 kg sodium nitrate, the mixture is rubbed through a sieve, introduced into the

reactor, to which 102 kg commercial sulfuric acid is added. This method was developed

by A.V.Stepanov (Bibl.153). Its chief shortcoming is the impossibility of utilizing

spent acid, as this sharply increases the cost of the product.

Aguiar (Bibl.170) produced trinitronaphthalene from dinitronaphthalene. To do

this, 100 gm 1,5-dinitronaphthalene was mixed with 1000 gm strong nitric acid at

120 - 130° for one hour in a reactor with a reflux condenser. The result of the

reaction was the production of 1,3,5-trinitronaphthalene.

F. Trinitrophenol and Other Nitro Derivatives of the Phenols

Trinitrophenol was first obtained in 1771 by Woulff by reacting nitric acid and

indigo (Bibl.183). Because of its acid properties and bitter taste (Πικροσ - meaning

bitter) was called picric acid. In 1813, the same product was obtained by Loran, by

the nitration of phenol. The comparatively accessible initial raw material made it

possible to organize the manufacture of picric acid, which was employed as a yellow dye

for wool and silk. At that time, the explosive nature of picric acid was not known.

In 1868 - 1869 it was proposed to employ the potassium and ammonia salts of picric

acid as a component of explosives made from potassium nitrate. In 1873 Sprengel

discovered that picric acid could be exploded by the use of a mercury fulminate

detonating cap. This made it possible to employ it independently to fill artillery

shells. It was found that, to explode cast picric acid, one needed an

intermediate detonator of pressed picric acid, which in turn would dependably detonate

due to the action of a mercury fulminate detonating cap.

Starting in 1886, picric acid came to be employed widely to fill shells in

174   France under the designation of Melinite, starting in XXXXXXXXXXXX 1888 in England

under the designation Lyddite, in Japan under the title of Shimose, in Germany under

the designation C/88 and in Russia, starting in 1896, under the designation Melinite.

Thanks to the fact that picric acid was the first explosive which, having high

black
power and brisance, was less dangerous to store and to handle than the XXXXX powders

hitherto known in military practice, nitroglycerin XXXXXX and pyroxylin, its manufacture

immediately was undertaken on a very large scale.

In Russia, the manufacture of picric acid was first XXXXXX undertaken in 1896 at

the Okhta Works (which burned in 1907) and somewhat later, during World War I, at

manufactured from phenol,
three other plants. At two plants, picric acid was XXXXXXXXXXXXXXXXXXXXX and at

the third from benzene, through dinitrochlorobenzene as intermediate (Bibl.184).

176   Toward the end of World War I, about 10,000 tons of picric acid was being manufactured

per year in Russia, 25,000 tons in Germany, and about 50,000 tons per year each in

Britain and France.

However, the scale of production of picric acid, XX even at the beginning of the

Twentieth Century, XXXXXXX began to XXXXXX diminish, as a consequence of its negative

properties such as reaction with the shell casing, resulting in the formation of

iron picrate, highly sensitive to shock, and the fact that it could not be employed

to ammonites.

At the present time, TNT has replaced picric acid almost in its entirety, and its

production in peace time has XXXXXXXX been sharply reduced. In wartime, the significance

of picric acid as an explosive remains. This is XXX testified to, in part, by

investigations in the field of XXXXXXXXXXXXXXXXXX rationalization of existing methods,

as well as the development of new methods of producing picric acid. Particularly great

176   attention has been given, in recent years, to producing picric acid directly from benzene, by the method of oxidizing nitration.

During World War II, a number of major scientists worked on the problem of a more profitable method of producing picric acid, to wit, by oxidizing nitration of benzene in the presence of a mercury~~xxxxx~~ catalyst. These scientists included N.G.Laptev and A.I.Titov (Bibl.185), and in the USA Dunning, ~~xxxxxxxx~~ Robertson, Westheimer, etc. (Bibl.186, 187).

In the course of World War II, 33,000 tons of picric acid was manufactured in Germany. In Japan, according to the data of Colley (Bibl.188), picric acid production was on a rather substantial scale.

Section 1. The Chemistry of the Production of Phenol Nitro Derivatives

Nitro derivatives of phenol and, in particular, trinitrophenol, are produced in industrial practice from phenol or benzene ~~xxxx~~ (via dinitrochlorobenzene as intermediate, or ~~xxxxxxxxxx~~ the nitration of benzene in the presence of mercury nitrate). Each of these methods enjoys ~~xx~~ certain advantages. In peacetime, they permit the manufacture of highly valuable intermediates in the form of dinitrophenol and ~~xxxxxxxxxx~~ dinitrochlorobenzene, which are widely employed in the manufacture of dyes.

a) Production of Trinitrophenol from Phenol

Phenol C_6H_5OH is a crystalline substance, colorless or pinkish, with a freezing point of 42.5^o and boiling point of 182°. The specific gravity of phenol at 50° is 1.0466. Its ~~thermal~~ capacity is 0.561 kcal/kg/^oC, and its latent heat of vaporization at the boiling point is 114 kcal/kg. The temperature of autocombustion of the fumes in air is 430°. .

Phenol constitutes from 10 - 25% of coal tar. The large demand for phenol on the

part of a number of branches of the chemical industry (plastics, aniline dye, lacquer

and paint, etc.) gave rise to the need for large-scale production of synthetic phenol.

Modern methods of phenol synthesis employed benzene as the starting substance.
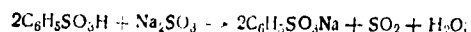
Phenol is produced in the following ways.

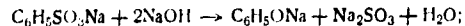1. By fusing the sodium salt of benzenesulfonic acid with caustic, the principal

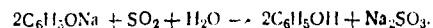stages of the process being:

a) sulfonation of benzene

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O;$$
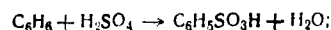
b) formation of the sodium salt of benzenesulfonic acid

$$2C_6H_5SO_3H + Na_2SO_3 \rightarrow 2C_6H_5SO_3Na + SO_2 + H_2O;$$

c) fusing of the sodium salt of benzenesulfonic acid with caustic soda:

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O;$$

d) decomposition of the phenolate

$$2C_6H_5ONa + SO_2 + H_2O \rightarrow 2C_6H_5OH + Na_2SO_3.$$

2. Hydrolysis of chlorobenzene by caustic, in accordance with the reaction

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O.$$

sodium phenolate
With subsequent decomposition of the ꞏꞏꞏꞏꞏꞏꞏꞏꞏꞏꞏꞏꞏꞏꞏ by acid (sulfuric or

hydrochloric)

$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl.$$

Hydrolysis is performed with a 10% aqueous caustic soda solution at 200 - 250 atm

pressure and 300 - 350°.

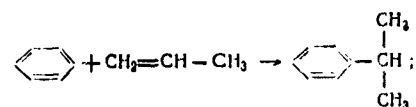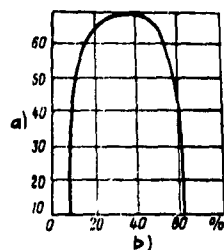3. Catalytic hydrolysis of chlorobenzene by steam. Hydrolysis of chlorobenzene

by steam

$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$$
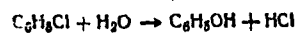
is performed at 450 - 500° over a catalyst (silica gel and others).

4. Decomposition of hydrogen peroxide of isopropylbenzene. Under this method,

two valuable products, phenol and acetone, are obtained simultaneously. The process is

run in stages:

a) production of isopropylbenzene (cumene) by

alkylation of benzene by propylene:

$$\langle \rangle + CH_2{=}CH-CH_3 \rightarrow \langle \rangle -\underset{CH_3}{\overset{CH_3}{CH}} ;$$

Fig.5? - Effect of Temperature

upon Solubility of Phenol

in Water

a) Temperature, in °C;

b) Solubility of Phenol

b) oxidation of isopropylbenzene by air

(in an aqueous alkaline emulsion under pressure

at 130°) with conversion (as the consequence of

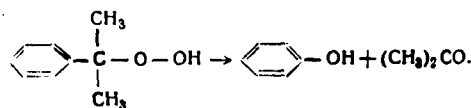a chain reaction) into the hydrogen peroxide

$$\langle \rangle -\underset{CH_3}{\overset{CH_3}{CH}} + O_2 \rightarrow \langle \rangle -\underset{CH_3}{\overset{CH_3}{C}}-O-OH;$$
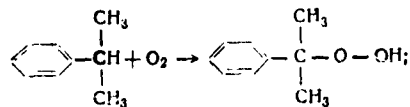
c) Decomposition of the hydrogen peroxide isopropylbenzene (by boiling in dilute

sulfuric acid under pressure) into phenol and acetone:

$$\langle \rangle -\underset{CH_3}{\overset{CH_3}{C}}-O-OH \rightarrow \langle \rangle -OH+(CH_3)_2CO.$$

Synthetic and coal-derived phenols contain cresols and other impurities. Phenol

designed to yield trinitrophenol should be a colorless or slightly pink crystalline

product with a freezing point at not less than 37°.

Phenol and water are mutually satisfactorily soluble (Fig.59). The critical

solution is
temperature of maximum 68.3° above which phenol and water will mix in any ratios.

Upon long contact with the air, phenol, undergoing oxidation, acquires a reddish tint,

177   and, upon absorption of moisture from the air, liquifies.

Phenol is weakly acid, and, upon reaction with bases, yields salts called

phenolates
~~phenolates~~. Thus, for example, it dissolves readily in aqueous solutions of caustic

soda and caustic potash with formulation of phenolate in accordance with the following

equation

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O.$$

Phenol does not react with soda.

In working with phenol, it must be borne in mind that it is highly poisonous and

heal
moreover, tends to eat away the skin upon contact, and causes ulcers that ~~heal~~ with

difficulty.

Phenol is considerably more reactive than benzene and toluere. It undergoes

sulfonation and nitrates readily. Nitration with weak nitric acid is an autocatalytic

process and is caused by the formation of nitrous acid as the product of secondary

reaction (Bibl.189).

178   When phenol is nitrated with nitric acid, a mixture of ortho- and para-nitrophenols

results. The temperature at which nitration occurs &X affects the composition of the

nitrophenols, and increase in temperature increases yield of the ortho-isomer(Bibl.190).

The reaction
~~The reaction~~ goes analogously when a mixture of sodium or potassium nitrate and dilute

sulfuric acid is employed for nitration (Bibl.191). Meta-nitrophenol does not come

into being upon direct nitration of phenol, and its production is usually from

meta-nitroaniline via the diazo compound.

Table 57 presents certain properties of nitrophenols.

As we see from Table 57, ortho-nitrophenol differs from the meta- and ~~para-nitrophenols~~

para-nitrophenols by the coloration of the crystals and the sharp odor. Moreover,

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Table 57

Chemical	Melting Point, °C	Boiling Point, °C	Appearance
Ortho-nitrophenol	45	214.5	Yellow crystals having a sharp odor similar to that of nitrobenzene
Meta-nitrophenol	96	194 at 70 mm Hg (with sublimation)	Colorless, odorless crystals
Para-nitrophenol	114	–	Colorless crystals, but a solution in alkali is colored yellow

as distinct from other isomers, it is readily distillable by steam. The cause of the coloration, according to Hantsch, is the tendency of ortho-nitrophenols to form acị forms:

$$C_6H_4 \underset{NOOH.}{\overset{O}{\diagdown}}$$
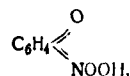
having a quinoid structure
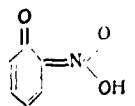
Phenols can be nitrated directly only by highly dilute acids. This is difficult and ~~absolute~~ unprofitable from the technical point of view. Nitration of phenol by a mixed acid even of middle strength (total acidity 70 - 75%) is, however, virtually impossible, as the high reaction velocity and, as a consequence, the rapid liberation of heat results in oxidation and resinification. To prevent these processes from taking place, the phenol is first sulfonated, to yield a less reactive compound - phenol sulfonic acid. Moreover, the nitration of the latter results in a lesser thermal effect than the direct nitration of phenol.

Sulfonation of phenol. When phenol is acted upon by sulfuric acid, one, two, and sometimes three hydrogen atoms of the sulfo group may be replaced in its molecule. The

178 number of entering sulfo groups depends primarily upon the strength and amount of acid

and, to a lesser degree, upon the temperature and reaction time.
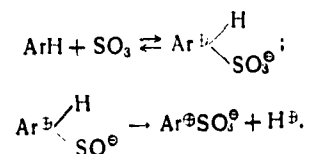
In accordance with the reaction equation

$$C_6H_5OH + H_2SO_4 \rightleftarrows C_6H_4(OH)(SO_3H) + H_2O$$

the sulfonation process accompanied by the formation of water, which dilutes the

sulfuric acid and, moreover, is reversible (Bibl.192). In accordance with the most

recent studies (Bibl.193), the active sulfonating agent in aqueous sulfuric

179 acid is the monomer of sulfuric anhydride (SO_3) or, possibly, the sulfate solvate

thereof, and, in oleum, also the dimer of sulfur trioxide (S_2O_6) which is present

there in the form of the solvate of trisulfuric acid.

These particles are formed in accordance with the following equations:

$$2H_2SO_4 \rightleftarrows S'O_3 + H_3O^+ + HSO_4^\ominus;$$
$$4H_2SO_4 \rightleftarrows S_2O_6 + 2H_3O^+ + 2HSO_4^\ominus.$$
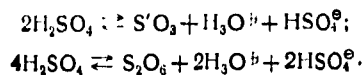
Sulfonation apparently goes in a manner similar to that of nitration, in two

stages:

$$ArH + SO_3 \rightleftarrows Ar \underset{SO_3^\ominus}{\overset{H}{\diagup}};$$

$$Ar \underset{SO^\ominus}{\overset{H}{\diagup}} \rightarrow Ar^\oplus SO_3^\ominus + H^+.$$

Melander (Bibl.194) found that, as distinct from nitration, sulfation is

accompanied by a noticeable hydrogen isotope effect: in the sulfation of benzene or

bromobenzene containing tritium, the proton is displaced by weak oleum

somewhat more rapidly than is the tritium. This testifies to the fact that the

second stage is quite slow as compared to the inverse direction of the first stage.

The velocity constants of the reactions of sulfonation and hydrolysis, and as a

consequence thereof, XY the equilibrium XXX constants depend upon the strength of the sulfuric acid (Bibl.195).

With reduction in the strength of the sulfuric acid, the sulfonation velocity constant diminishes, and the velocity constant of hydrolysis increases, although in less marked fashion. In this case, the equilibrium constant also diminishes. As a consequence of the significant diminution in the sulfonation velocity constant, the reaction virtually ceases at a particular concentration of the sulfonating agent. This strength of sulfuric acid, expressed in per cent of SO_3, has come to be denoted as the π XXXXXXXXXXXX of sulfonation.

The value of the π of sulfonation depends upon the nature of the compound being sulfonated, upon the temperature and degree of sulfonation, i.e., upon the number of sulfo groups entering.

The quantity of sulfuric acid or oleum x (in kg), required for monosulfonation XX XX of p kg of organic substance XXXXXXX with a molecular weight of M, may be computed on the equation

$$ x = \frac{80(100 - \pi) \cdot p}{(S - \pi) \cdot M}, $$

where S is the total concentration of SO_3 in the initial sulfonating agent. It is clear from the formula, that the higher the concentration of SO_3 in the initial sulfonating agent, the lower the quantity thereof required for sulfonation.

The π of sulfonation may be reduced by increasing the reaction time and, particularly, by increasing the sulfo acids content of the reaction mass. These, undergoing hydration, are bound by the water of reaction (Bibl.196).

For the monosulfonation of phenol, $\pi = 55\%$ SO_3, for disulfonation, it is 68% SO_3, and for trisulfonation it is 81.6% SO_3. In all three cases, the temperature at which

179   the material is held has to be 120° (Bibl.197).

In choosing the strength of the sulfonating agent and the temperature of

sulfonation, one must take into consideration the possibility that side processes

will occur. The employment of a sulfonating agent of high strength (containing

free SO_3) may result in the formation of sulfones:

$$ArSO_3H + HAr \rightarrow ArSO_2Ar + H_2\dot{O},$$

180   the obtaining of which is facilitated by the presence of the sulfonic acid, which is

already quite considerable in quantity, and by high temperature.

The high temperature of sulfonation may also induce oxidation. This is facilitated

by certain XXX catalysts such as Hg and Se (Bibl.198). In sulfonation, the oxidizing

effect is manifested both in the formation of oxy compounds, and in far-reaching

changes that may include the combustion of organic substances.

The temperature at which the sulfonation process occurs XX affects the position

of the sulfo group entering the compound. When sulfonation occurs in the cold, the

sulfo group enters in the ortho position. When it occurs at 100°, the sulfo group

enters in the para position. The heating of ortho-phenolsulfonic X oxide at 100°

converts it to para-phenolsulfonic oxide. This fact is made use of in production of

picric acid. Inasmuch as para-phenolsulfonic oxide nitrates at XXXXX higher speed

than ortho-phenolsulfonic oxide (Bibl.199), as a consequence, when phenol is

sulfated, the sulfo mass is held at 100 - 110° when the process comes to an end, for

the purpose of converting ortho-phenolsulfonic acid into para-phenolsulfonic acid.

The heat effect of reaction of sulfonation of aromatic compounds is less than

the effect of the nitration reaction. From this, we are able to understand the

convertibility
reversible nature of the sulfonation reaction, and the mutual XXXXXXXXX   of the

346

isomers of the sulfonic acids, as well as the possibility of ready substitution of the sulfo groups by the nitro groups.

The isomerization of the sulfonic acid is explained by the fact that the ortho-isomer is less stable to hydrolysis than the para-isomer. However, inasmuch as the rate of sulfonation is high in the ortho-position, when temperature is primarily this isomer that is formed. When temperature rises, the ortho-isomer undergoes hydrolysis, and the para-isomer is simultaneously formed. Under these circumstances, it does not undergo hydrolysis (Bibl.195).

Tables 58 and 59 illustrate the effect of the strength of the sulfuric acid, XX the length of XXXXXXXXXXX sulfonation time, and of temperature, upon the yield of phenoldisulfonic acids. In XXX all the experiments, 5 parts sulfuric acid by weight are taken per part of phenol by weight (Bibl.200).

Table 58

Percentage Strength of H_2SO_4	92	93	94	96	97	100
Yield of disulfonic acid per hr at 100°, %	62	66	71	82	91	100

Table 59

Time, hrs	Percentage Yield of Phenol Disulfonic Acid when Reacted with 93% H_2SO_4, at °C		
	75	100	150
0,25	--	48	50
0,5	51	65	66
1,0	59	66	66,5
2,0	—	68	—
4,0	—	68,5	—

It is evident from the data adduced that the best conditions for producing XXXXXX phenoldisulfonic acid are a temperature approximating 100°, and a sulfonation time XX of about 30 min.

180　　　　　An increase in the temperature to 150° has virtually no effect upon the yield of

disulfonic phenol, but, at the same time, it results in the formation of sulfones.

(Bibl.201).

When phenol is heated with ten times the quantity of 20% oleum at 120° for three

hours, a mixture of the ~~IXMX~~ di- and trisulfonic acids of phenol is produced (Bibl.202).

The sulfonation of phenol by 20% oleum results in the formation of 2,4- and 2,6-

181　　　　disulfonicphenol and partially, of trisulfonicphenol. 2,6-Disulfonicphenol readily

isomerizes at 100 - 110° to 2,4-disulfonicphenol. Therefore, in the manufacturing

　　　　　　　　　　　　　　　　　　　of phenol
process, when sulfonation/comes to an end, it is held at 100 - 110°, with the object

of converting the 2,6-disulfonicphenol to the 2,4-isomer, which then ~~XM~~ undergoes

freer nitration.

The sulfo derivatives of phenol usually are not separated from the sulfo mass,
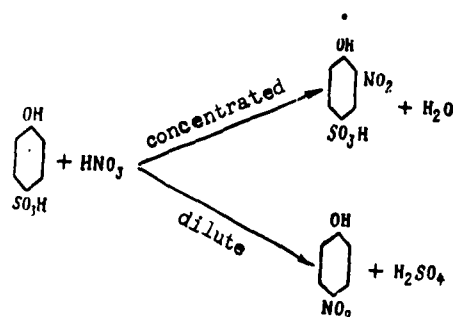
but undergo direct nitration.

In the pure form, the sulfo oxides of phenol are colorless crystals, which acquire

a reddish tint in air. They have ~~NMIXM~~ no characteristic melting and boiling points,

and, when heated, decompose with carbonization. Sulfonic acids readily dissolve in

water. They are strong acids and form two types of salts: sulfonates, in which the

　　　　　　　　　　　　　　　　　　replaced
hydrogen of the sulfo group is ~~XMMXMMM~~ by a metal, and phenolates, in which the

hydrogen of the hydroxyl group is replaced by a metal.

The sulfo group is readily neutralized even by carbonates. However, the hydroxyl

group in the monosulfonic acids is neutralized with difficulty by carbonates.
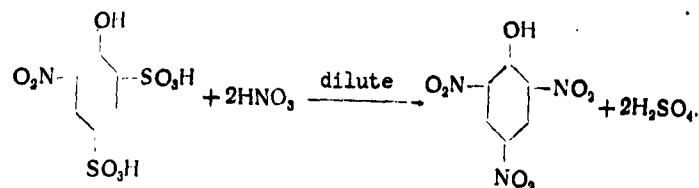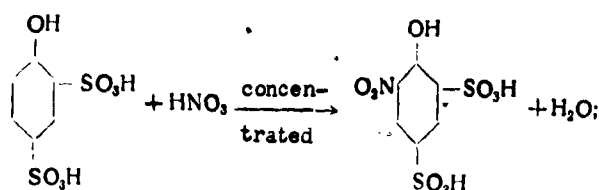
The acid properties of the sulfonic acids of phenol increase in the following

sequence: meta-, para-, ortho-phenoldisulfonic acids. Their susceptibility to

hydrolysis diminishes in the same order.

<u>Nitration of sulfonicphenol.</u> This process goes considerably more quietly than

the nitration of phenol, and is capable of being affected by mixed sulfuric and nitric

acid. The stability of phenol with respect to oxidizers increases when electrically

negative groups are present in the molecule. Therefore, when the degree of sulfonation

of phenol is increased, the yield of nitro derivatives rises, and the intensity of the

oxidizing processes diminishes.(Bibl.197, 200).

In dilute sulfuric acid, nitric acid exercises XXXXXXXXX an oxidizing effect

at elevated temperature, as a consequence of which oxalic acid is formed. Oxidation

goes the more noticeably, the less the degree to which the phenol ring is protected by

substituting groups. XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

King has shown (Bibl.199) that, when nitric acid acts upon phenolsulfonic acid

in the presence of excess strong sulfuric acid, the hydrogen in the ring is replaced

by a nitro group. In the presence of dilute sulfuric acid, the sulfo group is replaced

by nitro groups.

The introduction of the nitro group may be expressed by the following diagrams:

Consequently, when three nitro groups are introduced into the phenol molecule,

the most advisable procedure is to employ these regularities of the process in the

following order:

In this case, no acid circulation is required in the production of picric acid

from phenoldisulfonic acid. The most concentrated mixed acid is required at the

beginning of the process for the purpose of introducing the first nitro group.

Subsequently, the nitro mixture is diluted by water as a reaction product, rendering

the medium more favorable to substitution of a nitro group for the sulfo group. If

the nitration process is properly set up, it will go under the most favorable

circumstances: a homogeneous medium, thanks to the good solubility of sulfonic acids

and their nitro derivatives in sulfuric acid. At the end of the process, crystals

of a considerably more difficultly-soluble trinitrophenol will come down.

Disulfophenol nitrates at a lower rate than does phenol, and is more stable with

respect to oxidizing processes. Nevertheless, oxidation does occur upon nitration.

To reduce it, the temperature is held at not over 60°, in the introduction of the

first nitro group.

In the first stage of nitration, upon addition of 1 mole HNO_3 to mole of

disulfonic phenol, nitrodisulfonicphenol is formed:

$$C_6H_3(SO_3H)_2OH + HNO_3 \rightarrow C_6H_2(NO_2)(SO_3H)_2OH + H_2O.$$

The XXXXXXXXX 6-nitro-2,4-disulfonicphenol isomer is produced, as the bulk of

350

182   the sulfonicphenol consists of 2,4-disulfonicphenol. A certain quantity of 4-nitro-

2,6-disulfonicphenol is also formed from the 2,6-disulfonicphenol present in the

sulfo mass.

The effect of the second molecule of HNO_3, is that the SO_3H group is replaced

by an NO_2 group, and the two following isomers of dinitrosulphonic phenol result:
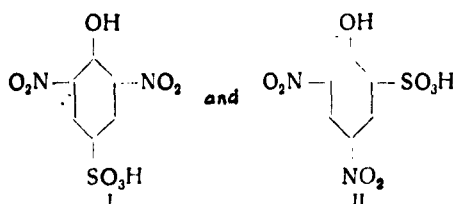
Both these isomers are formed from 6-nitro-2,4-disulfonicphenol, the former isomer

predominating. However, the 4-nitro-2,6-disulfoniphenol isomer yields only 4,6-dinitro-

2-sulfonicphenol. The formation of 4,6-dinitro-2-sulfonicphenol is undesirable, as its

further nitration goes only with difficulty. This is not to be avoided completely, but

the quantity diminishes as a consequence of conversion of 2,6-disulfonicphenol into

2,4-disulfonicphenol by holding the sulfo mass at 100 - 110° for some period.

With further nitration, both isomers of dinitro-sulfonicphenol converts to

picric acid, in accordance with the equation:

$$C_6H_2(NO_2)_2(SO_3H) OH + HNO_3 \rightarrow C_6H_2(NO_2)_3 OH + H_2SO_4.$$
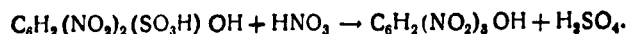
The second nitro group enters at 60 - 80°, and upon the introduction of the

third nitro group, the temperature rises to 100°. The mixture is held at the same

temperature. The high temperature of the nitration process results in a considerable

183   oxidation of nitrophenols to oxalic acid, which increases the consumption of nitric

acid by 20 - 25%, and substantially reduces the yield of XXXXXXXXXXXXXX nitro products.

The need to perform nitration at high temperature is induced by the difficulty

in converting 4,6-dinitrophenol-2-sulfonic acid to the trinitroderivative. The

incomplete denitrated product reduces the yield of picric acid and reduces its quality,

inasmuch as it is not possible to separate it completely from the nitric acid by washing

with water.

In the production of nitro compounds, it is desirable to replace oleum by

commercial sulfuric acid, as this makes it possible to set up a closed acid circulation.

After regeneration, the spent acid is reconverted to commercial sulfuric acid, which may

again be used for sulfonation of the phenol. In connection therewith, a process for the

production of picric acid without oleum was investigated, consisting of the following::

sulfonation is carried out by adding 91 - 91.3% commercial sulfuric acid to the molten

phenol at 40°, in a period of 5 - 7 min. The temperature rises at first as a consequence

of the heating reaction, and is then brought to 100 or 110° on an oil bath, and allowed

to stand at that level. The resultant sulfonicphenol, consisting of a mixture of mono

and disulfonic derivatives, the composition of which is indicated in Table 60, is

nitrated by melange to trinitrophenol.

Table 60

a)		1	2	3	4	5	6	7	8	9
b)		10	10	20	20	30	30	40	40	60
c)	mono-	74,7	44,4	—	43,5	58,0	44,2	57,3	40,7	—
	di-	25,3	55,6	—	56,5	42,0	55,8	42,4	59,3	—
d)	mono-	—	33,5	—	29,9	—	30,8	—	—	28,6
	di-	—	66,5	—	70,1	—	69,2	—	—	71,4

Note. In experiments 1,3,5, and 7, the temperature maintained was 100°, and
in experiments 2,4,6,8, and 9, was 110°.

a) Experiment number; b) Holding time, min; c) Composition of the sulfonicphenol, in %,
at a 1:5.4 ratio of phenol to sulfuric acid; d) Percentage composition of sulfonicphenol
at 1:7.5 ratio of phenol to sulfuric acid

183   In order to hold constant the amount of sulfuric acid produced in nitration, and

thereby to eliminate the effect of other factors upon the yield of picric acid, the

sulfonicphenol produced is diluted in the cold by commercial sulfuric acid. After

nitration, the spent acid contains 77.8% sulfuric acid. XX Under these conditions,

the yield of picric acid, regardless of the degree of sulfonation, is identical, and

comes to 83 - 84% of the theoretical. Consequently, the nitrability of monosulfonicphenol

upon identical acidity of the medium is the same as that of disulfonicphenol. This

circumstance compels one to assume that the factor influencing the yield of picric

acid is not so much the degree of sulfonation as the strength of the nitrating mixture.

Consequently, XX in the production of picric acid, oleum may be replaced by commercial

sulfuric acid, if we take the ratio of phenol to sulfuric acid monohydrate as 1:7.5.

This does not require the dilution of the sulfo mass by commercial sulfuric acid, as

is the case in sulfonation with oleum.XX

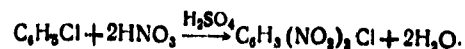b) Production of Trinitrophenol from Benzene via Dinitrochlorobenzene

The production of trinitrophenol from benzene requires several stages,

in accordance with the following equations.

1. Chlorination of benzene to chlorobenzene:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl.$$
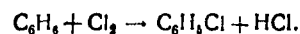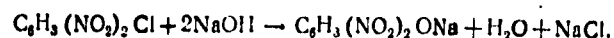
184   When benzene is chlorinated, the result is not only monochlorobenzene but

polychlorides. There is also a part of the benzene that does not go into the

chlorination reaction, and therefore the liquid obtained in chlorination is to be

divided by distillation, in order to emerge with comparatively pure monochlorobenzene.

2. Nitration of monochlorobenzene to dinitrochlorobenzene by fixed sulfuric and

nitric acid:

$$C_6H_5Cl + 2HNO_3 \xrightarrow{H_2SO_4} C_6H_3(NO_2)_2Cl + 2H_2O.$$

3. **Saponification of dinitrochlorobenzene, to sodium dinitrophenolate:**

$$C_6H_3(NO_2)_2Cl + 2NaOH \rightarrow C_6H_3(NO_2)_2ONa + H_2O + NaCl.$$

4. **Production of dinitrophenol by treatment of sodium dinitrophenolate by sulfuric acid:**

$$2C_6H_3(NO_2)_2ONa + H_2SO_4 \rightarrow 2C_6H_3(NO_2)_2OH + Na_2SO_4.$$

5. **Nitration of dinitrophenol to trinitrophenol by mixed sulfuric and nitric acid:**

$$C_6H_3(NO_2)_2OH + HNO_3 \xrightarrow{H_2SO_4} C_6H_2(NO_2)_3OH + H_2O + 12,9 \; Kcal \, / \, mole$$
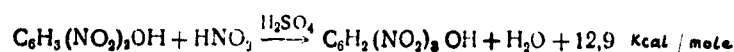
The polychlorides obtained as by-products in the chlorination of benzene are

purified and employed for the production of dyes, and the hydrogen chloride liberated

is trapped by water and used to produce hydrochloric acid. Chlorination of benzene

is performed by gaseous chlorine in the presence of a catalyst – iron chloride, the

strength of which in the benzene should be 0.01 – 0.015%. The iron chloride, XKMX may
either be introduced
XXXXXXXXXXXXXXXXX into the benzene delivered to chlorination or produced directly

in the reactor. To accomplish the latter, iron is placed in the reactor, and is

converted to $FeCl_3$:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3.$$
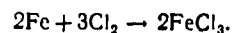
In accordance with modern concepts, the catalyst promotes the formation of

positively charged ions of chloride in accordance with the following mechanism

(Bibl.203)

$$FeCl_3 + Cl_2 \rightleftarrows FeCl_4^{\ominus} + Cl^{\oplus}.$$
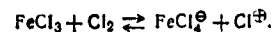
The $Cl^{\oplus}$ ion reacts subsequently with the aromatic compounds:
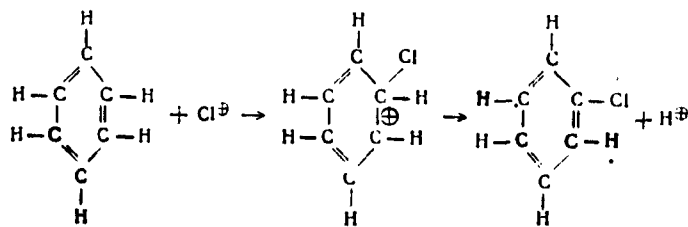
184   The proton reacts with $FeCl_4^-$, recovering the catalytically active salt $FeCl_3$, and

forming hydrogen chloride:;

$$FeCl_4^\ominus + H^\oplus \rightleftarrows FeCl_3 + HCl.$$
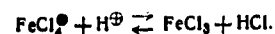
In accordance with the mechanism presented, the catalyst acts only upon the

chlorine. However, the action of the catalyst upon the aromatic compound is also

possible. This is testified to, in part, by the effect of the nature of the catalyst

upon the ratio between the chlorine derivative isomers.

185   When benzene is chlorinated in the presence of iron chloride, the process goes

in the direction of formation of chlorobenzene only at the very beginning:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl,$$
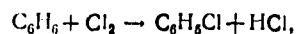
but later, the chlorobenzene formed converts to dichlorobenzene:

$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl.$$
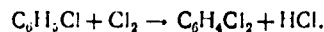
The yield of chlorobenzene (in terms of benzene) approximates 100% at the onset

of chlorination. As the reaction progresses, it continually declines, inasmuch as,

as the concentration of chlorobenzene increases, the rate of conversion thereof into

dichlorobenzene becomes greater than the rate of formation.

To avoid the formation of a large quantity of polychlorides, it is desirable to

stop the chlorination reaction when the concentration of chlorobenzene attains

32 - 50%. In this situation, the polychlorides formed constitute not more than 5%

of the resultant monochlorobenzene by weight.

The chlorination reaction is monitored by determining the specific gravity of the

reaction mixture.

The temperature of chlorination influences the formation of polychlorides. The

temperature coefficient of the chlorination rate of benzene is 8 or 9% lower than that

355

185 of chlorobenzene. Therefore, with increase in temperature of chlorination, more

polychlorides are formed.

Previously, the chlorination process was carried out by a batch-wise method at

20 - 25°. Today, chlorination is performed by a continuous method at the boiling point

of the reaction mixture (76 - 83°). This makes for intensive loss of heat of reaction

due to partial evaporation of benzene and chlorobenzene from the boiling mass.

Inasmuch as the chlorination reaction is exothermic (about 28 kcal are released per

mole of chlorine), the output rate of chlorators depends, for all practical purposes,

upon the rate at which heated reaction is removed. Therefore, chlorators XX that

function under conditions of boiling of the reaction mixture show a higher rate of

output than the ordinary type.

For purposes of chlorination, the benzene and chlorine should be as dry as possible,

as the hydrogen chloride formed in reaction, upon dissolving in water, rapidly decomposes

the catalyst   and the apparatus.

Drying of the benzene is usually performed by means of azeotropic distillation,

and drying of the chlorine by passing it through sulfuric acid.

Chlorobenzene is separated from the chlorinated benzene by distillation, which

presents no great difficulties in view of the great difference in the boiling point of

the components, constituting chlorinated benzene: 80.4° for benzene, 132° for

chlorobenzene, and 172 - 180° for polychlorides. Prior to distillation, the chlorinated

benzene is treated with dry soda or limestone, followed by filtration. This is necessary

in order to remove hydrogen chloride, which may induce corrosion.

Chlorobenzene (monochlorobenzene) consists of a colorless, mobile liquid smelling

of almonds. It is not soluble in water, but dissolves well in alcohol, ether, benzene,

185   chloroform, and carbondisulfide. The boiling point of chlorobenzene is 132.2°;

the freezing point is 45.2°; specific gravity is 1.106 gm/cm^3 at 25°. The temperature

is 0.31 kcal/kg/°C. Chlorobenzene is hot, and emits hydrogen chloride when heated.

·Its chemical activity is lower than that of the halide-substituted hydrocarbons

of the aliphatic series. Chlorobenzene reacts with ammonia only when heated in an

                                                                       Strong
autoclave to 180 - 200° in the presence of copper salts or pulverized copper.XXXXX

aqueous solutions of caustics cleave chlorine away from chlorobenzene only at

300°. The strength of the bond between the halide and the ring is diminished

upon introduction of NO_2 and the COOH XXXXXX group into the ring. Chlorine is

activated with particularly high degree by these groups which are in the ortho-

186   and para-position with respect thereto. Chlorobenzene is slightly narcotic.

Table 61 presents some of the physical properties of the polychlorides, which

are also produced in the chlorination of benzene.

Table 61

a)	b)	c)	d)
1,4 -dichlorobenzene (para-)	52,69—53,2	171—174	at 20°—1,3581
1,2-dichlorobenzene (ortho)	14	179	at 19°—1,3039
1,3-dichlorobenzene (meta-)		—	at 25°—1,2835
	e)		
1,2,3-trichlorobenzene	53—54	212—219	—
1,2,4-trichlorobenzene	17	205—213	at 10°—1,574
1,3,5-trichlorobenzene	53,4	208,5	—
1,2,3,4-tetrachlorobenzene	45—46	254	—
1,2,3,5-tetrachlorobenzene	50—51	246	—
1,2,4,5-tetrachlorobenzene	137—138	236—246	at 175°—1,3958
Pentachlorobenzene	84—86	275—276	at 81°—1,6095
Hexachlorobenzene	222,5	322—332	at 203°—1,519

a) Isomers; b) Melting point, °C; c) Boiling point, °C; d) Specific gravity;

e) Freezes in a mixture of water and ice

Nitration of chlorobenzene to dinitrochlorobenzene goes in two stages. First,

the first nitro group is introduced at a temperature of 45 - 50°. The result of

357

nitration is a mixture of ortho-, para-, and meta-nitrochlorobenzene. The formation

of the meta-isomers is undesirable, as upon further nitration,/converts to
it

asymmetrical trinitrophenol. The yield of meta-isomer depends upon temperature.

The higher the temperature of nitration, the higher the yield of meta-isomer.

Certain of the physical properties of nitrochlorobenzene are presented in

Table 62.

Table 62

a)	b) ·	c)	d)
Freezing point, in °C	32,5	46,0	83,0
Boiling point, in °C	245	235	242

a) Nitrochlorobenzene isomers; b) Ortho-; c) Meta-; d) Para-

Nitrochlorobenzene is subjected to further nitration to dinitrochlorobenzene

at 75 - 80°. 2,4-dinitrochlorobenzene (or α-) is a virtually

colorless crystalline substance with a freezing point of 53.4°. The 2,6- or

β-isomer freezes at 43.2°, and the 3,5-, or γ-isomer, at 27°. The technical

product consisting chiefly of α-isomer has a freezing point of 46 - 47°,

inasmuch as it contains impurities. The chief impurities are 2,6- and

3,5-dinitrochlorobenzene, as well as the ortho-, para-, and to some degree, the

meta-nitrochlorobenzenes, and 3,4-dinitro-1-chlorobenzene. The quantity of the

latter depends upon the temperature conditions of the first stage of nitration. The

higher the temperature of the first stage, the greater the yield of the undesirable

3,4-dinitro-1-chlorobenzene.

In addition to the impurities cited, dinitrochlorobenzene contains considerably

358

smaller quantities of dinitrobenzene and nitropolychlorides. These impurities

187   are formed in the nitration of benzene and the polychlorides contained in the

initial chlorobenzene.

Dinitrochlorobenzene is virtually insoluble in cold water and is slightly

soluble in hot water. 100 gms of water dissolve the following quantities of

dinitrochlorobenzene, in gms:

at 15° 0,0008
at 50° 0,0410
at 100° 0,1590

Its solubility in 85% sulfuric acid (in %):

at 20° . . . . about 1,7
at 50° . . . . about 4,0
at 70° . . . . about 6,5

degree of
This/solubility of dinitrochlorobenzene results in considerable losses thereof,

inasmuch as the spent acid contains 85% sulfuric acid. These losses may be

eliminated by employing acid circulation, i.e., by utilizing the spent acid in

the first-stage nitration.

Table 63 presents the solubility of dinitrochlorobenzene in organic solvents.

Table 63

a)	b)		
	15	30	50
Ethyl alcohol	8,2	18,8	—
Methyl alcohol	11,2	32,3	—
Ethyl ether	23,5	128,3	—
Chloroform	102,7	210,0	—
Ethyl acetate	119,4	—	297,5
Toluene	139,9	282,5	—
Benzene	153,1	339,5	—
Acetone	267,9	—	531,0

a) Solvent; b) Solubility, gms (per 100 gms of solvent) of dinitrochlorobenzene, at the following temperatures, °C

A mixture of dinitrochlorobenzene and strong mixed acid is heated for 12 hrs at 130°, the result is picryl chloride, with a yield of 85% of theoretical (Bibl.204).

Dinitrochlorobenzene is readily saponified by bases, and forms dinitrophenolates. When it is saponified in the presence of alcohols, the consequence is ethers, such as dinitrophenetol, dinitroanisole etc.

In working with dinitrochlorobenzene, it must be borne in mind that its fumes are powerful irritants of the mucous membrane, and therefore the workshops must have good ventilation.

2,4-Dinitro-1-chlorobenzene is used to manufacture sulfur dyes. It condenses with a large number of compounds in the aromatic series, and the condensation products produced are reduced by sodium sulfide and sulfur.
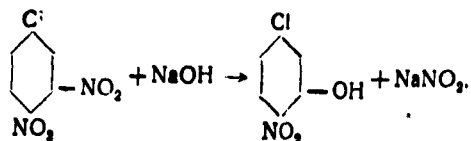
As already indicated, 2,4-dinitro-1-chlorobenzene is saponified by bases, to yield sodium dinitrophenolate:

$$C_6H_3(NO_2)_2Cl + 2NaOH \rightarrow C_6H_3(NO_2)_2ONa + NaCl + H_2O.$$
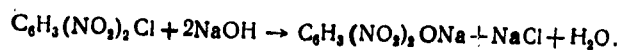
The reaction goes at high velocity even when weak alkali solutions are

employed. The ease with which chlorine is substituted for by the hydroxyl

is due to the presence in the ~~MAINX~~ molecule of dinitrochlorobenzene, of two

nitro groups, in the ortho- and para-positions with respect to chlorine. The

chlorine atom in chlorobenzene is saponified with difficulty by bases (the

reaction will occur in an autoclave at a temperature of about 300°, and with

strong caustic soda). Introduction of the nitro group into chlorobenzene activates

the chlorine atoms. Even in the ortho- and para-nitrochlorobenzene, the chlorine

atom is fairly easily exchanged for the hydroxyl, under the influence of a base.

~~TXX~~ A nitro group in the meta-position with respect to the chlorine, does not

activate it, and meta-nitrochlorobenzene usually does not saponify a caustic.

The saponification reaction of 2,4-dinitro-1-chlorobenzene is accompanied by

the emission of heat, and this may induce a pronounced rise in temperature. To

avoid processes of oxidation and possible flare-ups, the saponification of ~~XXX~~

2,4-dinitrochlorobenzene is performed at $100 - 105^{\circ}$ by a weak aqueous alkaline

solution (7%) used in very slight excess ~~excess~~ (1 - 2%) over the theoretically necessary.

Certain impurities in dinitrochlorobenzene - the ortho- and ~~XXXXXXXXXXXXXXXXXXXXXX~~

para-dinitrochlorobenzenes, are also saponified by caustic, and convert, ~~XXXX~~

correspondingly, to ortho- and para-nitrophenolates, which subsequently undergo

transformation to ~~XXXXXXXX~~ picric acid. 3,4-Dinitrochlorobenzene reacts with caustic,

but this is accompanied by an exchange not of the chlorine, but of the nitro group

in the meta-position with respect to the chlorine, for hydroxyl, the consequence

being ~~XXXXXXXXXX~~ 1-chloro-4-nitrobenzene, in accordance with the reaction:

$$\text{(structure)} -NO_2 + NaOH \rightarrow \text{(structure)} -OH + NaNO_2.$$

Subsequently, upon nitration of dinitrophenol to trinitrophenol, this compound diminishes the quality of the latter.

As already indicated above, meta-nitrochlorobenzene does not saponify, but remains in the dinitrophenol as an impurity. Reduction in the quantity thereof may be achieved by increasing the period of time at which the reaction mixture is held at 105° toward the end of saponification, the meta-nitrochlorobenzene being driven off by steam under the circumstances.

Sodium dinitrophenolate is readily decomposed by dilute sulfuric acid, with liberation of dinitrophenol, in accordance with the reaction:

$$2C_6H_3(NO_2)_2ONa + H_2SO_4 \rightarrow 2C_6H_3(NO_2)_2OH + Na_2SO_4.$$
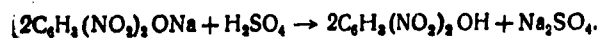
2,4-Dinitrophenol is a crystalline substance, bright yellow in color, having a freezing point of 112.5°, and a specific gravity of 1.683 (at 24°). The freezing point of 2,6-dinitrophenol is 62.5°. The 2,4-isomer crystallizes out of boiling water XXX in the form of small platelets or in the form of pale yellow or, sometimes, completely colorless needles. When carefully heated at 70°, dinitrophenol undergoes slow volatilization. It can also be driven off with water vapor. Its solubility in 100 gms of water is, in grams:

at 8°	0,014
at 18°	0,507
at 100°	4,78

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The solubility of dinitrophenol in organic solvents is illustrated in Table 64.

Dinitrophenol is acid in its properties and reacts with metals, oxides thereof, and carbonate salts, to yield dinitrophenolates, which are less sensitive than the corresponding picrates. With bromine, dinitrophenol forms dinitrobromophenol, melting point 119°.

189   Dinitrophenol is very toxic. It is essential that health and safety rules be adhered to when working with it.

Table 64

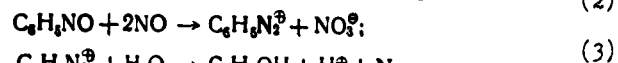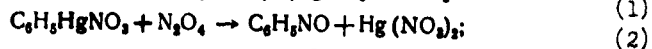| a)	b)	
	15	50
Pyridine	20,1	71,0
Acetone	35,9	98,3
Ethyl acetate	15,5	39,5
Benzene	6,4	25,7
Toluene	6,3	19,9
Chloroform	5,8	19,8
Methyl alcohol	4,9	16,9
Absolute ethyl alcohol	3,0	11,3
Ether	3,1	7,2
Carbon tetrachloride	0,4	1,8
Carbon disulfide	0,4	1,0

a) Solvents; b) Solubility (in 100 gms of solvent) of dinitrophenol, in gms, at the following temperature, °C

As an explosive, dinitrophenol is similar to dinitrobenzene. It is not employed by itself. During the First World War, an alloy of 40% dinitrophenol and 60% picric acid was employed in France.
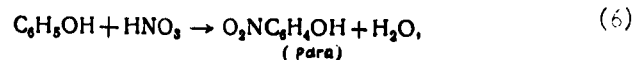
363

c) <u>Production of Trinitrophenol from Benzene by Oxidizing Nitration in the Presence of a Promoter</u>

The production of trinitrophenol from ~~XXX~~ benzene by nitration of the

latter with weak nitric acid in the presence of mercury nitrate as promoter has

been
~~XXXX~~ investigated by many scientists (Bibl.205, 206, 207). The most complete

studies in the mechanization of this process, as well as its practical realization,

are due to A.I.Titov and N.G.Laptev (Bibl.185).

Oxinitration
~~XXXXXXXXXX~~ (oxidation and nitration) of benzene to 2,4-dinitrophenol and

to 2,4,6-trinitrophenol by mercury nitrate in nitric acid goes through the

following stages:

$$C_6H_6 + Hg(NO_3)_2 \rightarrow C_6H_4HgNO_3 + HNO_3; \qquad (1)$$
$$C_6H_5HgNO_3 + N_2O_4 \rightarrow C_6H_5NO + Hg(NO_3)_2; \qquad (2)$$
$$C_6H_5NO + 2NO \rightarrow C_6H_5N_2^{\oplus} + NO_3^{\ominus}; \qquad (3)$$
$$C_6H_5N_2^{\oplus} + H_2O \rightarrow C_6H_5OH + H^{\oplus} + N_2; \qquad$$
$$C_6H_5OH + HNO_3 \rightarrow O_2NC_6H_4OH + H_2O, \qquad (4)$$
$$(\text{ortho}) \qquad (5)$$

or

$$C_6H_5OH + HNO_3 \rightarrow O_2NC_6H_4OH + H_2O, \qquad (6)$$
$$(\text{para})$$
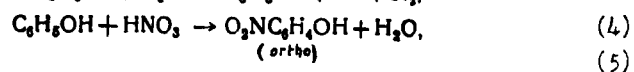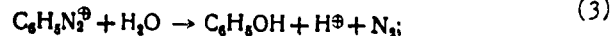
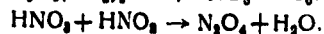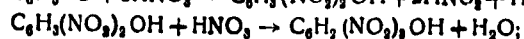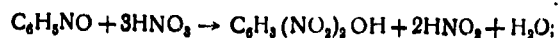subsequent to which the mononitro derivatives are nitrated further.

(3)
A.I.Titov and N.G.Laptev regard reaction ~~XXXX(X)~~ and those which follow

it (4) and (5) as not being the basic ones. According to their views, the basic

190 reactions subsequent to the decomposition of the mercury derivative and the

formation of nitrophenol are the following:

$$C_6H_5NO + 3HNO_3 \rightarrow C_6H_3(NO_2)_2OH + 2HNO_2 + H_2O;$$
$$C_6H_3(NO_2)_2OH + HNO_3 \rightarrow C_6H_2(NO_2)_3OH + H_2O;$$
$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O.$$

According to the mechanism envisaged by A.I.Titov and N.G.Laptev, the total

~~XXXXXX~~

expenditure of nitric acid in the formation of one mole of trinitrophenol is 5 moles, and one mole of the dimer nitrogen dioxide,is formed simultaneously.

Production of trinitrophenol by this mechanism is carried out by circulation of benzene through 50% nitric acid, containing 3.5% mercury nitrate. The reaction occurs at 50°. The benzene, saturated with nitro derivatives, and having a specific gravity of not less than 1.2, is removed from the cycle. The spent benzene is heated at 60° for 24 hrs, and the dinitrophenol is nitrated by the nitrogen oxides in the benzene to picric acid. Upon completion of the reaction, the mixture is cooled to 5 - 7°, and the crystallized picric acid is filtered off the benzene, which is returned to the cycle.

A necessary condition for introducing oxidizing nitration into production is regeneration of the mercury. Only if this problem is satisfactorily solved can oxidizing nitration successfully compete with other methods (Bibl.208).

Section 2. Properties and Applications of Trinitrophenol

Picric acid or 2,4,6-trinitrophenol is a crystalline substance existing in two polymorphic forms. The crystals obtained from the alcohol solution are orthorhombic in shape, bright yellow in color, having a freezing point of 121.3° and a melting point of 122.5° (Bibl.183). The specific gravity of crystalline picric acid is 1.763, and that of the liquid acid is 1.589 (at 124°).

The gravimetric density if 0.9 - 1.0, and the density of the cast picric acid is 1.61 - 1.67. Pressing at a pressure of 2000 kg/cm^2 yields a density of 1.63. By increasing the pressure to 4125 kg/cm^2, it becomes possible to increase density to 1.74. The latent heat of fusion of picric acid is 20.4 kcal/kg, and the specific thermal capacity of 0.234 cal/gm. Picric acid is virtually non-hygroscopic. When

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XXXXX fused, it volatilizes to a limited degree: vapor pressure 195° - 2 mm Hg,

and at 225° - 50 mm Hg (Bibl.183).

picric
Tables 65 - 67 illustrate the solubility of XXXXXX acid in water and other

solvents.

Table 65

a)	b)	a)	b)
0	1,05	40	1,98
5 .	1,07	50	2,53
10	1,10	60	3,17
15	1,16	70	3,89
20	1,22	80	4,66
25	1,37	90	5,49
30	1,55	100	6,33

a) Temperature, °C; b) Solubility, g of picric acid XXX in 100 gms water, gm

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Table 66

a)	b)		
	18	50	80
0	1,184	2,389	4,541
2,3	0,0230	0,692	1,940
4,7	0,142	0,368	1,251
10,0	0,091	0,265	0,727
18,0	0,049	0,214	0,561
25,5	0,092	0,230	0,587
50,5	0,429	0,645	1,104
69,7	0,928	1,424	2,203
87,9	2,461	5,826	7,610
97,4	7,532	12,785	24,024
100,0	10,180	16,230	25,860

a) Strength of sulfuric acid, %; b) Solubility, gm, of picric acid (in 100 gms
acid), at temperature, °C

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Table 67

a)	b)											
	15	20	27	35	38	42	48	51	56	60	65	78
c)	—	5,9	—	—	—	—	—	—	—	—	—	40
d)	—	3,45	—	—	—	—	—	—	—	8,4	--	—
e)	—	28,3	—	33,3	—	38,3	—	42,5	46,2	—	—	—
f)	9,1	—	12,3	14,3	16,7	—	22,7	—	29,4	—	39,7	—
g)	6,8	8,8	11,4	17,6	—	23,5	—	—	33,5	—	41,7	50

a) Solvent; b) Solubility of picric acid, %, at temperatures in ^{C}C; c) Alcohol;
d) Dichlorobenzene; e) Nitrobenzene; f) Dichloroethane; g) Benzene

Picric acid dissolved in ether, methyl alcohol, glycerin, chloroform, carbon disulfide, and also in resins and lacquers. The solubility of picric acid in water and in sulfuric acid is of practical interest. In view of its considerable solubility in water, hot water cannot be employed to wash picric acid.

Aqueous solutions of picric acid are yellow in color, while solutions of picric acid in sulfuric acid and ligroin are colorless. A similar phenomenon occurs in the cultivation of crystals of picric acid. Ordinary industrial picric acid is yellow, but picric acid recrystallized from sulfuric or hydrochloric acid is virtually colorless.

Certain hypotheses exist with respect to the reason for the coloration of picric acid. It is held that undissociated picric acid is colorless, but that the $[C_6H_2(NO_2)_3O]^{\ominus}$ ions are yellow. Other views hold that the coloration of nitrophenols, including picric acid, depends upon the fact that they exist in two tautomeric forms: the benzoid and the quinoid:

benzoid form   quinoid form

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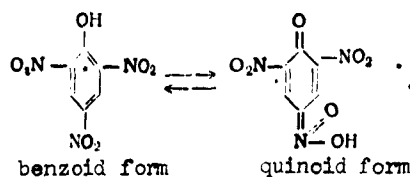
Both these forms are in equilibrium, and the equilibrium is shifted in the direction of formation of the quinoid form. The quinoid form of picric acid is colored, and the benzoid is colorless. In the opinion of Hantsch, as already indicated, salts of the nitrophenols have the quinoid form.

Picric acid and its solutions color tissues of animal origin (wool, silk, hair, ~~XXXXXXX~~ skin) yellow. As is the case with other nitro compounds, they form complexes that crystallize well (Bibl.209); for example, with naphthalene, they form golden yellow crystals having the following composition $C_{10}H_8$ $C_6H_2(NO_2)_3OH$. This reaction is frequently employed to separate picric acid.

A characteristic reaction for picric acid is provided by KCN, which forms isopupuric acid with it. This is a red compound (qualitative determination of small quantities of picric acid).

Upon reduction, picric acid converts to triaminophenol. This reaction is employed to get rid ~~XXXX~~ of the picric acid in wash waters as otherwise they dirty and poison bodies of water.

Nitric acid dissolves picric acid, and virtually does not react with it (Bibl.210). Bleaching lime converts picric acid, in the presence of water, to chloropicrin $CCl_3(NO_2)$ (a poison).

Picric acid is a somewhat stronger acid than carbonic acid. It reacts with carbonates to liberate ~~XXX~~ CO_2 and form picrates. In the presence of moisture, picric acid decomposes cellulose and glycerol ~~XXXXXXX~~ nitrates, as well as ammonium nitrates, cleaving HNO_3 away ~~XXXXXXX~~ therefrom. Therefore, it can be used in a mixture with these components. In the presence of moisture, picric acid reacts with virtually all metal: other than tin and the ~~XX~~ noble metals), yielding salts

(picric). Picric acid reacts with metal oxides or carbonates salts more

readily ~~than~~ with metals (Bibl.211).

    The majority of picrates are more soluble in water than is picric acid,

but, nonetheless, they are not soluble in dry benzene. This property is

employed to determine picrates in picric acid.

    All picrates are solid crystalline substances having substantially greater

sensitivity to water and friction than does picric acid. The greatest sensitivity

is that of lead and iron picrates. In sensitivity, lead picrate is similar to

lead azide. Minimum sensitivity is displayed by the picrates of sodium and

ammonium. The latter is employed to fill shells. The shock sensitivity of

picrates is illustrated in Table 68.

Table 68

a)	b)	c)	a)	b)	c)
Picric acid	95	300	Iron picrate	7	300
			Lead picrate	5	260
Sodium picrate	80	360	Silver picrate	5	—
Zinc picrate	60	315	Lead azide	4	—
Copper picrate	7	310	Mercury fulminate	2	210

a) Explosive; b) Height from which weight is dropped (2 kg), cm; c) Detonation point,^{o}C

    In the process of production of picric acid, picrates may come into being

in the washing and drying process, as a consequence of the presence of salts in

the wash water. Salts reacting with picric acid yield picrates, which remain in

the picric acid in greater quantity, the more poorly the separation was

193   performed. Therefore, the washing of picric acid should be performed with soft

water (not containing salt), and before it is sent to drying, the product should

be thoroughly centrifuged from the wash water on a hard-rubber or

XI

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tin-plated centrifuge. To avoid the formation of picrates as washed picric

acid contacts metal, the washing and drying portions of the apparatus should

~~should~~ preferably not be of metal, or, in any case should consist of certain

particular metals (aluminum, tin-plated copper, bronze).

The possibility that picrates may be formed by direct reaction between picric

acids and metals in the process of nitration is eliminated by the presence of

sulfuric acid in the nitro mixture. The formation of picrates may occur upon

reaction of picric acid with alkali earth bases and salts in cement floors, and

therefore cement must not be used for flooring in picric acid production.

When the aqueous solution of picric acid is saturated with ammonia, ammonium

picrate results.

Ammonium picrate is a crystalline substance (yellow or red in color, in

different modifications), having a specific gravity of 1.72, fusing at $265 - 270°$

(Bibl.183), and having a detonation point of $290°$. Ammonium picrate dissolves

readily in boiling water (74.8 gm per ~~in~~ 100 gm water at $100°$) and less satisfactorily

in cold water (1.1 gm per 100 gm water at $20°$). It is considerably more

hydroscopic than picric acid, and when stored in a moist ~~MM~~ atmosphere for a

month, absorbs more than 5% water. It is insoluble in benzene. Completely dry

ammonium picrate undergoes virtually no reaction with metals and their oxides,

whereas moist ~~XXXXXXX~~ picrate reacts, but more slowly than does picric acid.

Ammonium picrate is a comparatively unstable substance, and when heated to

$220°$, vigorous decomposition, with liberation of ammonia, sets in:

$$C_6H_2(NO_2)_3 ONH_4 \rightleftharpoons C_6H_2(NO_2)_3 OH + NH_3.$$
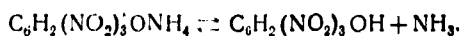
This reaction also proceeds at a lower temperature. If ammonia be removed

from the reaction sphere, considerable decomposition of ammonium ~~XXXXXX~~ picrate is possible

accumulation
. (and consequently, XXXXXXXXXXXXX of picric acid when it is stored for a long

period in conditions other than airtight).

picrate
In the United States, ammonium XXXXXXX is produced on the industrial scale

in the following way: when heated, one part picric acid per weight is dissolved

in 10 - 12 parts water per weight, to which 20% ammonium picrate is added until

complete neutralization is achieved (0.4 - 0.5 parts per weight), and upon cooling,

ammonium picrate XXXXX comes down, which is filtered, washed, and dried.

Ammonium picrate does not react with salts, inasmuch as the hydrogen of the

Previously,
hydroxyl group therein has already been replaced by the NH_4 group. XXXXXXXXX

XXXXXXXX
ammonite of the following composition: 72% NH_4NO_3 and 23% picrate ("gromoboy" or

"maisite") was manufactured on ammonium picrate as base.

Ammonium picrate is less shock-sensitive than picric acid. It detonates

when a weight of 2 kg is dropped from a height of 100 cm. The heat of explosive

decomposition is 800 kcal/kg, and the rate of detonation (at $\Delta = 1.63$) is

7150 m/sec (Bibl.183).

demolition shells
In the United States, XXXXXXXXXXXXX armor-piercing and fragosholls used

to be XXXXX filled with ammonium picrate (by the method of pressing).

Picric acid also forms picrates with organic bases. Thus, for quantitative

determination of picric acid, employment is made of acridine picrate

benzene,
$C_{13}H_9N \cdot C_6H_2(NO_2)_3OH$ which is poorly soluble in water, XXXXXXX and alcohol.

Quantitative determination of picric acid may be formed with the aid of nitron,

with which picric acid yields a picrate poorly soluble in water.

194 . Picric acid is poisonous, and therefore the appropriate safety rules have

to be adhered to in working with it.

In the pure form, picric acid is very stable to the usual temperatures of

storage. A small quantity thereof may even be subjected to volatilization by

heating to 125 - 130°. At 160°, one observes slight decomposition of picric

acid with liberation of gases, and deflagration occurs at 300 - 310°. Ignited

picric acid burns slowly, with a smoky flame, in the open air or in wooden

packaging.

When hot used picric acid is brought into contact with iron, slaked lime,

or salt solution, and the like, the entire mixture explodes, as a consequence,

apparently, of the formation of highly-sensitive picrates. To avoid this, the

walls of storehouses and factory buildings housing this material must be covered

with a gypsum plaster, and electrical equipment must not include either lead

or iron, ~~XXXXXXX~~ but only ~~XXXXX~~ aluminum or copper, as these metals form compounds

with picric acid only with difficulty.

Upon rapid heating in an enclosed shell, to 300°, picric acid explodes.

explodes when a 2 kg
Picric acid is ~~XX~~ more sensitive than TNT to shock. It ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXXX~~

weight is ~~XXXXXX~~ dropped from 80 cm, whereas TNT requires dropping from 100 cm.

sensitivity
Because of the comparatively high shock ~~XXXXX~~ of picric acid, the pure

product is employed only to fill small and medium-caliber shells. Large-caliber

shells are filled with mixtures of picric acid and ~~XXXXXXXXXXXX~~ dinitronaphthalene.

Addition of silica considerably increases the sensitivity of picric acid to

shock, as is evident from Table 69.

Table 69

a)	b)	c)
0	25	25
0,25	25	60
0,50	25	100

a) Percent silica sand in picric acid; b) Number of tests (10 kg weight ZZXXMIXXZX 25 cm height); c) Complete explosions, %

In the pressed or cast form, picric XIX acid is less shock-sensitive than in the XXXX powder form.

When pulverized picric acid is subjected to friction between plates of hard metals (iron, steel) and stones it explodes.

The explosive properties of picric acid are as follows: volume of gases 730 ltr/kg, heat of explosion 1050 kcal/kg, temperature of explosion $3300 - 3500^{\circ}$, expansion in Trauzl block 305 cc, Hess brisance 16 mm, rate of detonation 7350 m/sec.

Picric acid is employed both in the pure form and in mixtures with nitro compounds to fill munitions. The addition of nitro compounds IXXXXX the reduces sensitivity of picric acid to mechanical influences and XXXXXXX permits the filling of large-caliber shells with alloys thereof.

The most widely employed picric acid alloys were: the French mixture (80% picric acid and 20% dinitronaphthalene) having a melting point of 104°, and the Russian mixture (51.5% picric acid and 48.5% dinitronaphthalene) having a melting point of $82 - 87^{\circ}$, and also an alloy consisting of 60% picric acid and 40% dinitrophenol (melting point 85°), and an alloy consisting of 60% trinitrocresol

and 40% picric acid (melting point 85°). The use of readily fusible alloys

makes it possible to fill shells with molten explosives without having to heat

them excessively.

During World War II, picric acid was employed in Germany to fill hand

grenades, detonators, aircraft bombs (in the form of a mixture with

dinitronaphthalene) and certain special shells (explosive smoke shells).

When picric acid is employed to fill shells, special attention must be given

to providing complete isolation thereof from the shell casing and the detonator.

This was previously done by covering the interior of the shell with tin plate or

lacquer. This method does not provide a complete guarantee of isolation of the

picric acid, because of the difficulty of monitoring the quality of the covering.

A more reliable method is the cartridge-type of filling. The explosive charge of

picric acid is placed in a paperboard or some other nonmetallic container and is

XXX thus kept divided from the shell casing. Assembly of the two into a unit is

performed not too long a time prior to the employment of the shell. The Japanese
used
XXX this method XX as far back as the Russo-Japanese War.

Section 3. Technology of Trinitrophenol Production

a) Production of XXX Picric Acid from Phenol

The method of obtaining picric acid from phenol was developed and widely

employed on an XXXXXX industrial scale as far back as the last century. Subsequently,

this method underwent considerable XXXXXXXXXX technological changes. The major

improvement was employment, for sulfurization   and subsequent nitration, of

phenol instead of weak acids (92% sulfuric and 45% nitric acid), XXXXXXXX strong

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acids (oleum and melange). The use of strong acids made it possible to ~~MAXXX~~

employ cast iron ~~XXXXXX~~ instead of ceramics for the apparatus. The use of

in making
metal ~~XXXXXXXXXXXXX~~ the apparatus, in turn, made it possible to make them of

more advanced design. Apparatus came to be produced with mechanical agitators,

as well as with jackets and coils for the delivery of coolant water therein.

This facilitated the attainment and sustaining of precise conditions of temperature.

The production of picric acid consists of the following operations: ~~XXXX~~

sulfonation
1) ~~XXXXXXXXXX~~ of the phenols; 2) nitration of the phenol sulfonic acid; 3) separation

of the product from the acid and washing with water; 4) drying of the washed picric

into
acid; 5) separating ~~XXXXXX~~ batches and packaging of the finished product.

Moreover, there are usually special workshops to purify the wash water and the

spent acids.

The production of picric acid from phenol in batch-type apparatus is

diagramed in Fig.60.

The phenol is carried, in zinc-plated drums, on cars (1) and is raised to

the top ~~stamp~~ of the building by means of an elevator (2). The drum is placed in

a melting device (3), provided with a jacket into which steam is emitted. As fusion

of the phenol occurs, it flows through a hole in the bottom of the drum and through

the bottom flange of the melting device into a metering tank (4), which stands on

scales. The metering device is provided with a coil for delivery of steam so as

to keep the phenol in molten condition.

Sulfonation is performed in a sulfurator (5), which is a cylindrical cast-

bottom and
iron vessel with a spherical ~~XXXXXX~~ cover, and provided with a steam jacket. The

sulfurator contains a coil for water, and an impeller agitator for stirring. A

375

specific quantity of oleum (computed in terms of II-sulfonation) is charged ~~XII~~ via the measuring tank (6), and the phenol is added slowly, over the course of an hour, with the agitator in operation. The phenol is run in under conditions of a gradual increase in temperature from 20 to 90°. Upon completion of the

196   run-in,~~XI~~ the mixture is held at 100° for 3 hrs, then is sent to the collector (7), and then to the metering tank (8), for delivery to the nitrator (11).

Monitoring of the sulfonation process is performed by observation of the sulfonation temperature and analysis of the sulfo mixture for acidity, which, after holding, should not be less than 64% in terms of H_2SO_4.

                                                          in
The process ~~XIX~~ of nitration is performed ~~XX~~ apparatus of the ~~XXXXXX~~ same design as sulfurator. The nitrator is made of cast iron. The solution of
                                                              by
disulfophenol is charged into nitrator (11), and spent acid (2.13 parts ~~XXX~~ weight per part phenol by weight) is run in from metering tank (10), for dilution, inasmuch as formation of the picric acid yields a mass so thick as to render
                                              oxides,
difficult the ~~XXX~~ escape of the nitrogen ~~XXXXXX~~ with the consequence that the mass foams. Nitration is by melange, which is run in from metering tank (9). The amount of melange is calculated to ~~XXXXX~~ deliver 3.75 gm-moles HNO_3 per 1 gm-mole phenol. The total melange is divided into three parts, in a ratio of 4:4:5, run in at various temperatures. The first part begins to be run in at 40°, and run-in terminates at 60°; run-in of the second part is terminated at 80°, and of the third part at 100°. During the third stage of nitration, after approximately 2/3 of the melange has been run in, crystals of picric acid starts to come down. Run-in continues for about 3 hrs.

Upon completion of run-in, the mixture is held for 1 hr at 100°, whereupon

the contents of the apparatus are cooled to 30°, and are transferred through

collector (12) to funnel (13), which serves to supply the centrifuges. Settling

out of the acid from the product and of the mechanical impurities from the acid

is performed therein over a period of 10 - 12 hrs. As settling occurs, the

picric acid floats to the top, while the spent acid accumulates at the bottom

of the funnel, and the mechanical impurities (mineral salts and others) settle at

the bottom of the funnel. After settling, a portion (60 - 65%) of the spent acid

is let out of the funnel into collector (21). All the mechanical impurities that

have settled out are dumped along with the acid.
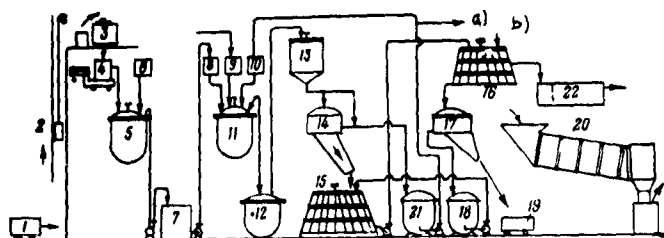
Fig.60 - Diagram of Production of Picric Acid from Phenol

1 and 19 - Cars; 2 - Elevator; 3 - Melting device; 4, 6, 8, 9, and 10 - Measuring

tanks; 5 - Sulfurators; 7, 12, 18 and 21 - Collectors; 11 - Nitrator; 13 - Settling

funnel; 14 and 17 - Centrifuges; 15 and 16 - Decanters; 20 - Drying drum; 22 - Trap

a) Acid to recovery; b) Water

After the discharge of a portion of the spent acid from the funnel, the

stirrer is started, and the remaining turbid mass of spent acid, along with the

picric acid, is discharged to ▨▨▨▨▨▨▨ centrifuge (14), where the spent acid is

centrifuged away from the product. The centrifuged acid goes to collector (21),

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unloaded
and the picric acid is ~~XXXXXX~~ into decanter (15) (a wooden tank), into which acid

wash water had previously been run from collector (18), this being the water from

the washing in the previous operation.

The contents of decanter (15) are stirred with a mechanical wooden agitator,

and the acidity of the water rises to 3 - 3.5% due to the spent acid remaining

in the picric acid. The picric acid, which is turbid in the acid water, is

pumped to the ~~XXX~~ upper decanter (16) where it is permitted to settle for

197   10 - 15 min, and the wash water, having an acidity of 3 - 3.5% (minimum solubility

of picric acid) and being ~~XXXX~~ in a quantity of 3 parts by weight to one part by

weight of product, is discharged through the upper drainage flange to trap (22),

from which it goes to purification. After discharge of the acid water, pure water

weight),
is run into decanter (16) (2 parts by weight per 1 part product by ~~XXXXXX~~ the

mass is mixed, and discharged to ~~XXXXXXXXX~~ centrifuge (17), where the water is

separated from the ~~XXXX~~ picric acid, and ~~XXX~~ it is washed once again with cold

water (1 part water by weight to 1 part product by weight). The wash water is

collected in collector (18), and is used for first washing.

Thus, water circulation is employed in the washing of picric acid. The

consumption of water is 3 tons per 1 ton of picric acid, with the consequence

that there is a considerable ~~XXXX~~ reduction in picric acid losses in washing.

At some plants, the washing of ~~XX~~ picric acid is performed in a somewhat

difference fashion.

The acid product is charged into a decanter, into which acid water from

the preceding second washing of product and final washing on the centrifuge has

previously been run in. The product is mixed in the decanter, then permitted to

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settle, and the acid water is discharged through the upper flange. Fresh water

is then added, XX heated to 90°, and the entire mass is stirred at this temperature

for 1 hr, whereupon it is cooled, and the product is permitted to settle out of the

acid water. After the second washing, the acid water is run into a receiver, and

the product is discharged into a centrifuge. On the centrifuge, the product is

separated from the acid water, and washed with fresh water. The wash water goes

from the centrifuge to the receiver, and is mixed with water from the second

washing of the picric acid. This water is then employed for the first washing.

Thus, the washing is performed in a single decanter, also with return water.

The second method of washing picric acid permits a reduction in the acidity

of the product (to less than 0.1%), thanks to the use of hot water, and simultaneously

improves its quality. This method of washing was employed chiefly in the production

of picric acid from benzene, through the dinitrochlorobenzene intermediate.

The spent acid, having settled out in collector (21), is employed in part

to dilute sulfophenol, whereas the rest goes to recovery and further to denitration.

The product, having undergone a final centrifuging on centrifuge (17), is discharged

into car (19) and transported to the drying division.

Picric acid, after washing, should be of not more than 0.1% acidity, or more

than 10% MXIXXXXXX moisture content. It is dried in drum drier (20).

designing
In XXXXXXXX driers for the drying of picric acid, it is necessary to bear

in mind that this acid reacts with metals and forms picrates. Therefore, wood

or aluminum, which do not react to picric acid, are the preferable materials for

the desiccators.

Ceilings in these buildings are made of wood, and roofs are covered with

tar paper. Concrete must not be used, inasmuch as picric acid, being stronger

than silicic acid, displaces SiO_2 in the concrete from its compounds of metals, to

form picrates (Ca, Mg, Fe, Na, and others) which may be caused for accidents. A

strong shock or friction causes the picrates to flash, and this may result in a

fire or explosion. Floors should also preferably be made of wood, covered with

XIX linoleum, which facilitates washing of the floor and protects the wood against

permeation by picric acid.

The dried picric acid is hauled in boxes on cars to the packaging department,

where it is sieved through copper mesh and packaged in wooden boxes or containers

198   lined with paper. The yield of picric acid is 85% of theoretical. Picric acid

has to satisfy the technical specifications indicated in Table 70.

Table 70

Property	Grade 1	Grade 2	Grade 3
Appearance (all grades)	Crystalline powder, without XX mechanical impurities		
Color	Bright yellow		
Freezing point, °C, less than	119,5	119,5	119
Benzene-insoluble residue, %, not more than	0,2	0,3	1,0
H_2SO_4 content, %, not more than	0,1	0,2	0,3

a) Properties; b) Grade 1; c) Grade 2; d) Grade 3

The quality of the picric acid is determined by the XXXXXXX purity of the

initial phenol.(absence of cresols XXXXXXXX therefrom), and also by the lack

of incompletely nitrated dinitrophenol. The quantity of impurities insoluble in

benzene may be increased by the dinitrophenol sulfonic acid (not converted into

picric acid) which undergoes partial dissolving in the picric acid.

. Spent acid, of the following percentage composition, is a picric acid

byproduct:

H_2SO_4 . . . . 77 - 79

HNO_3 . . . . 0.1 - 1

N_2O_3 . . . . 4 - 5

Oxalic acid . . . . 1 - 1.5

Dinitrosulfophenol . . . . 0.5 - 1.5

Picric acid . . . . 1.5 - 2

Water . . . . residue

This spent acid must not be sent directly to denitration, as, upon

denitration and concentration, the picric acid will be ꓒꓮꓲ𝅘𝅥𝅮ꓲ volatilized

and will deposit upon the apparatus and piping, which may be a cause of accident.

As a consequence, the spent acid is subjected to special cleaning, before

denitration, with the object of extracting the nitro products. Usually, they

are extracted by organic solvents.

A second 𝅘𝅥𝅮ꓮꓲꓲꓮꓲ waste product of picric acid production is the wash water,

which contains as much as 1.8% picric acid in solution and suspension. This water

is of substantial toxicity, and therefore it must undergo purification before being

dumped into bodies of water (Bibl.212).

In industry, the spent water is purified by reduction of picric acid to

triaminophenol by iron filings. 5.4 gm iron filings are consumed in the reduction

per 1 ltr of/water containing 0.4% picric acid. At a temperature of 15 - 20° the

wash

process is completed in 8 - 10 min. The triaminophenol obtained as a result of

reduction is then oxidized by atmospheric oxygen, with destruction of the benzene

ring. To perform reduction by iron filings, the acidity of the wash water must be

ꓘꓲ

no less than 7 - 8%, i.e., the water going to purification must be acidified.

It is usually acidified with spent acid. The purification process is illustrated

in Fig.61.

The wash water is delivered to receiver (2) and acidified with spent acid

from the pressure tank (1). Agitation during acidification is by means of

compressed air. Usually two such tanks are provided, which work alternately. The

199   acidified wash water is delivered from them by pump, continually, through metering

device (3), to apparatus (4) for reduction.
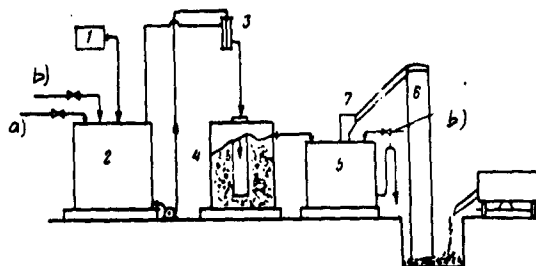
Fig.61 - Diagram of Purification of Spent Water

1 - Pressure tank; 2 - Receiver; 3 - Metering device; 4 - Apparatus for
reduction; 5 - Neutralizer; 6 - Elevator; 7 - Hopper
a) Wash water; b) Compressed air

The reduction apparatus is an ordinary cylindrical wooden tank containing a

wooden pipe that does not reach to the bottom. The tank is filled with iron filings.

The water enters the upper portion of the pipe, passing through it to the bottom

of the apparatus, and rises through the iron filings, going out of the upper portion

of the apparatus.

From the reducer, the acid water goes to a wooden neutralizer (5), where it

is neutralized with lime. The lime is delivered continually, in controlled quantity,

by elevator (6) through hopper (7). ~~XXXXXXXX~~ Agitation in the neutralizer is

·performed by compressed air. The purified water goes from the neutralizer through

a system of traps into the sewerage system.^{H} The process of purification is run

at normal temperature.

b) <u>Production of Picric Acid from Benzene through Dinitrochlorobenzene as</u>
   <u>Intermediate</u>

·The production of picric acid through dinitrochlorobenzene as intermediate

should be organized at plants that manufacture chlorine and are near benzene plants.

This makes it possible to chlorinate the benzene with gaseous chlorine, without

necessitating large expenditures to compress chlorine and transport it in cylinders.

The production is performed in four major departments: the chlorobenzene, the

dinitrophenol, the picric acid and the picric-acid drying.

<u>Chlorobenzene department</u>. Figure 62 illustrates the production of chlorobenzene

(Bibl.213, 214).

Benzene from tank (1), and gaseous chlorine, are delivered to the lower portion

chlorinator (2). The chlorinator
of the ~~chlorinator (2) the chlorobenzene~~ is a ~~XXXXX~~ steel column with acid-resistant

lining, having a packing of steel and ceramic rings. The upper (wider) part of

chlorinator
the ~~chlorinator~~ serves as a spray-catcher, and the ~~XXXXXXXX~~ hydrogen chloride formed

in chlorination is removed from its very top, along with benzene and chlorobenzene

fumes. The amount of benzene vaporized is 1.4 - 1.5 ton per 1 ton of

chlorobenzene obtained.

chlorinator
The gases emitted from the ~~chlorinator~~ are sent to a reflux condenser (3) with

graphite tubes impregnated with ~~XXXXXXXXXXXXXXXX~~ phenol-formaldehyde resin. Here

the gases and ~~XXX~~ fumes are cooled to 30°, and about 90% of the benzene contained

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in the vapors condenses. The benzene is separated in separator ~~XXXX~~ (4), and

the remaining fumes and gas go to a mixing condenser (5), where they are cooled

200   to -2°. More than 9% additional benzene is separated thereby.

packed
The mixing condenser is a ~~XXXXXXX~~ column through which the chlorobenzene

flows. The benzene fumes condense, and the solution of benzene and chlorobenzene

flows out of the bottom of the ~~XXXXXXX~~ apparatus. A portion of the solution is

h. cur(?)
~~again directed~~ to flow through the mixing condenser via condenser (7). Benzéne

is separated from the other portion of the solution in fractional distillation

column (8). In order to prevent the chlorobenzene from becoming saturated with

the condensing benzene, which may result in solidification of the solution upon

fresh
cooling, ~~XXXXXX~~ chlorobenzene is added to the circulating solution in collector (6).

From the chlorinator (2), the reaction mixture goes with the solution taken

off condenser (5), to separation in a two-column fractionating unit, employing a

continuous process. The mixture, entering fractionating column (8), contains

64 - 65% benzene, 33.5 - 34% chlorobenzene, about 1.5% polychlorides, and a small

amount of dissolved hydrogen chloride and ferric chloride. At some plants, the

reaction mass is treated with a weak solution of caustic alkali before fractionation,

to neutralize the HCl and decompose the $FeCl_3$.

The temperature in the vat part of column (8) is maintained within the limits

of 133 - 141°, and in the upper portion, within 75 - 88°. The distillate driven

off the column contains 99.5% benzene and 0.5% chlorobenzene. Raw chlorobenzene,

containing 0.15 - 0.25% benzene and 3.5 - 4.5% polychlorides flows directly from

the vat portion of the column. Commercial chlorobenzene is driven off the raw

material in column (12). The resultant chlorobenzene contains 0.3 - 1.1%

384
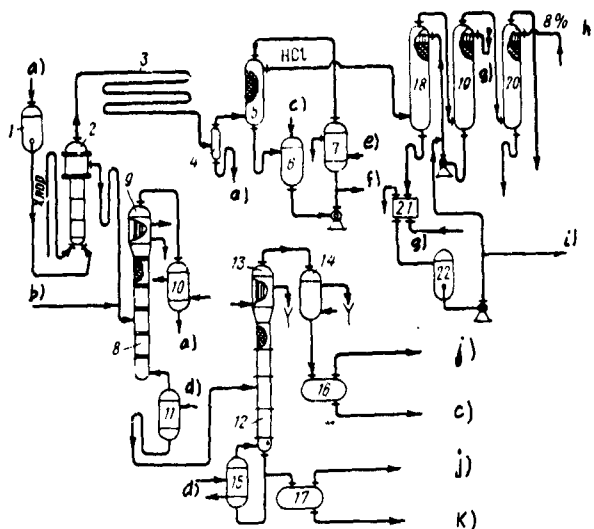
Fig.62 – Diagram Showing Continuous Chlorination of Benzene

1 – Pressure tank; 2 – Chlorinator; 3 – T̶r̶i̶p̶l̶e̶ Trickle condenser; ⅜ 4 – Separator;
5 – Mixing condenser; 6 – Intermediate collector; 7 – Condenser; 8 and 12 – Fractional
distillation; 9 and 13 – Fractionating column; 14 – Condensers; 11 and 15 – Boilers;
16 and 17 – Vacuum collectors; 18 and 19 – Absorbers; 20 – Neutralizing column;
21 – Graphite condenser; 22 – Sulfuric acid collector

a) Benzene; b) From apparatus (5); c) Chlorobenzene; d) Steam; e) Lime;
f) To apparatus (8); g) Water; h) ⅜ 8% caustic solution; i) Hydrochloric acid;
j) To vacuum pump; k) Polychlorides

polychlorides and about 0.3% benzene. The chlorobenzene content of the mixture

of polychlorides flowing out of the column vat usually ̶M̶A̶X̶ does not exceed 10%.

This mixture may be employed to produce tetra- and hexachlorobenzene.

201   Hydrochloric acid is obtained from the hydrogen chloride formed on chlorination.

To do this, the hydrogen chloride ̶e̶m̶i̶t̶t̶e̶d̶ discharged from the mixing condenser (5) goes to

three column-type apparatus connected in ̶s̶e̶r̶i̶e̶s̶ series (18), (19), and (20), of which the first

two (in the direction of gas flow) ̶(̶1̶8̶)̶ ̶(̶1̶9̶)̶ (18) and (19) serve as absorbers, whereas neutralization

385

of the residual hydrogen chloride occurs in apparatus (20). Absorber (18) is

irrigated with dilute hydrochloric acid. The strong hydrochloric acid emerging

from it is cooled to 20 - 30° in the graphite condenser (21). A portion of the

strong hydrochloric acid is returned to absorber (18) to increase the density of

irrigation.

The gases emitted from absorber (18) are sent to the second absorber (19)

for absorption of the residual hydrogen chloride. The resultant dilute hydrochloric

acid goes to irrigate absorber (18) . To neutralize the residual hydrogen chloride,

the gas is sent to column (20), irrigated by an 8% aqueous solution of caustic.
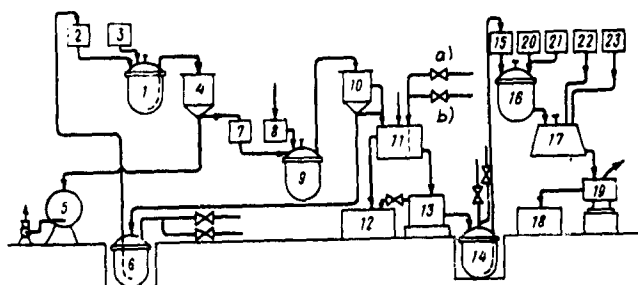
Fig.63 - Diagram of Production of Dinitrophenol from Benzene

1 - Extractor; 2,3,7,8,15,20,21,22,23 - Metering tanks; 4,10, and 13 - Separators;

5 - Receiver; 6 and 14 - Rising devices; 9 - Nitrator; 11 - Washing vat;

12 and 18 - Traps; 16 - Saponifier; 17 - Apparatus for decomposition of

sodium dinitrophenolate; 19 - Centrifuge

a) Steam; b) Compressed air

Dinitrophenol Shop. The production of dinitrophenol from chlorobenzene may

be formed in accordance with the mechanism illustrated in Fig.63.
    performed

In extractor (1), which is an iron vat enclosed in a jacket, spent acid is

charged in from metering tank (2), and cooled to 45°. Then, chlorobenzene (1 part

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per 2.5 parts spent acid) is gradually added from measuring tank (3). During

the charging period, the temperature is adjusted so as not to rise above

55 - 60°. After run-in and mixing to follow it, the extractor contents are

transferred to separator (4) over a 20 min period. The purpose of the operation

is the chlorobenzene extraction from the spent acid of the dinitrochlorobenzene

dissolved therein (about 2 - 5%). and utilization of the residual HNO_3

(1.5 - 2%).

The spent acid remaining in the separator is sent to receiver (5), and

from there to denitration, and the utilized ("stirred") chlorobenzene is sent

to measuring tank (7) for nitration. Nitration of the chlorobenzene to
dinitrochlorobenzene
is performed in a single stage. To accomplish this, a nitro

mixture consisting of 65 - 66% H_2SO_4, 28 - 29% HNO_3, and 5 - 6% H_2O. is

poured into nitrator (9) from measuring tank (8).

The amount of mixture is determined on the basis of 10% excess HNO_3 over the

theoretical. The chlorobenzene is added to the nitro mixture over a 3-hr period,

with temperature rising slowly from 20 to 45°. Upon completion of the run-in,

the nitro mass is heated for an hour to 105 - 110°, and then held at that temperature

another 30 min. At the end of the operation, the dinitrochlorobenzene must be

solidified at a temperature not below 47°.

202   Upon completion of nitration, the contents of the apparatus are forced into

separator (10) by compressed air (this is a cylindrical vessel with a conical base),

and are permitted to stand for 3 hrs. The dinitrochlorobenzene that
                                                                with a connecting piece
settles out of the spent acid is drained, by means of a valve to the

washing vat (11) and the spent acid goes to the rising device (6) from which it

is delivered for ▓▓▓▓▓▓▓ extraction.

The washing vat (11) has a bubbler , with steam and compressed air attached.

Water is run into the vat, which is then heated by live steam to 70°, whereupon

the dinitrochlorobenzene is run in (1.5 part water per part dinitrochlorobenzene).

After agitation by compressed air, and settling, the wash water is drained and

fresh water is run into the vat. Four such washings are made, ▓▓▓▓▓▓ followed by

one or two
a fifth with soda (3% solution), and then another ▓▓▓▓▓ water washings (until the

of the
residual acidity ▓▓▓▓ product is 0.02%).

The wash waters go to trap (12) and the dinitrochlorobenzene to separator (13),

for the fullest possible separation from the water. The separator (13) has a coil

for heating. Settling is performed at a temperature of 70 - 80°. After settling

for an hour to free it from water, the product is sent to ▓▓▓▓▓▓▓▓ saponification by

rising device (14). The saponifier (16) is an iron pot with jacket or coil for

heating, and an impeller agitator. Water heated to 75°, and a 25 - 30% caustic

solution are run into the saponifier from metering tanks (20) and (21). Caustic

calculated
soda is in 85% ▓▓ excess over the theoretical, and the ▓▓▓▓ water is ▓▓▓▓▓

to yield a 7.5% NaOH solution for saponification.

Because of the exothermic reaction involved in saponification, the temperature

rises to 93 - 95° during the run-in of dinitrochlorobenzene from ▓▓▓ metering tank (15).

The mixture is then heated to 100° and held there until saponification is completed

(20 - 30 min).

The completion of saponification is monitored by a sampling for t▓▓ absence of

dinitrochlorobenzene, which is performed as follows: ▓▓ 5 cc phenolate is dissolved

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in ███ cc hot water, and acidified with 10% sulfuric acid until acid reaction

is observed. If drops of oil appear at the bottom of the test tube, this will

testify to the presence of dinitrochlorobenzene. The absence of drops of oil

indicates that saponification ██ has been concluded. A second control is

titration with free caustic, the strength of which should be 0.4 – 0.8%.

In order to decompose the sodium dinitrophenolate, the mixture, at temperature

100°, is discharged from the saponifier into apparatus (17), consisting of a wooden

vat with coil, lead bubbler , and agitator. Water ██ and spent acid from picric

acid production is run into the apparatus beforehand from measuring *tank* ████ (22) and

(23). In order to bring about decomposition, spent acid, in 8% excess over the

theoretical, and water calculated to yield a 10% sulfuric acid solution, are

employed. Sodium dinitrophenolate solution, from the saponifier, is charged into

the sulfuric acid solution over a 25 min period, with stirring. After this run-in,

the mixture is held for 20 min at 75°. The operation is monitored by determining

the acidity of water in the bath, which/not *should* be less than 0.3%.

When the holding period is completed, the apparatus contents are ███ cooled by

water (via a coil) to 35°. Further cooling to 25 – 30° is performed by addition of

cold water to the apparatus.

Upon conclusion of the operation, the ██ mixture in the apparatus is drained

to centrifuge (19), running at low speed, where it is washed with water, after which

the centrifuge is switched to high speed for better removal of the water. The

centrifuged water goes to trap (18). The dinitrophenol, having a moisture ██ content

of 10 – 13% goes to picric acid production.

Picric acid is produced by nitration of dinitrophenol in an ordinary batch-type

iron nitrator (Bibl.215). Spent acid and 20% oleum is charged into the

nitrator in quantities calculated to yield a 94 - 95% sulfuric acid (2.5 parts

medium per part dinitrophenol by weight), whereupon the ~~MMIMM~~ moist dinitrophenol is

run-in. The apparatus contents are heated to 30°, whereupon, over a period of

3 - 3.5 ~~yrmx~~ hrs the nitrating mixture is run-in, and the temperature at the end

of the period of run-in is raised to 55°. The acid nitrating mixture has the

following composition: 71 - 72% H_2SO_4 and 28 - 29% HNO_3. It is run in to yield

a 50% excess of nitric acid over the theoretical. After the mixed acid has been

run-in, the reaction mixture is slowly heated for 1 - 1.5 hrs to $110 - 112^{\circ}$, and

held at that temperature for 1.5 hrs. It is then cooled to 30° over a period of

2.5 hrs, and removed by compressed air to the settling funnel. After settling,

a portion of the spent acid is discharged into a receiver, and the remaining spent

acid, along with the picric acid, is sent to a centrifuge or ~~Nutsch~~ suction filter.

The further treatment is identical with that described in our heading

"Production of Picric Acid from Phenol".

In Germany, nitration of chlorobenzene is performed in two stages in batch-type

apparatus. After the dinitrochlorobenzene has been produced, the spent acid is

~~MMMMXIMXMX~~ utilized in its entirety for nitration of chlorobenzene. After nitration of the

chlorobenzene, the spent acid is ~~MM~~ extracted by the latter, and goes to

denitration and concentration. The consumption data per ton of dinitrophenol are:

1.2 ton dinitrochlorobenzene, 0.43 ton caustic soda, and 0.26 ton sulfuric acid.

Nitration of dinitrophenol is performed in batch-type apparatus. 96 - 98%

Sulfuric acid, and dinitrophenol, are ~~MMMXI~~ run into the apparatus (bath /module 3:1)

subsequent to which mixed acid consisting of 51% H_2SO_4 and 49% HNO_3 is run in

gradually at 45°. Upon the conclusion of nitration, the reaction mixture is

diluted with water and the picric acid is separated from the dilute spent acid

on a ~~suction filter~~. The picric acid is then washed with water and dried on a rack

~~IIIIIII~~ desiccator. In order to extract picric acid from the spent acid, it

undergoes chlorobenzene extraction and then goes to denitration. The chlorobenzene

employed for extraction is treated with a ~~II~~ soda solution to remove picric acid

~~IIIIIII~~ therefrom in the form of sodium ~~IIIIIIIII~~ picrate.

The consumption data per ton of picric acid are: 0.86 ton dinitrochlorobenzene,

2.85 ton sulfuric acid, 0.36 ton nitric acid, and ~~III~~ 0.05 ton chlorobenzene.

Section 4. Nitrophenol Ethers

The desirability of employing ethers and in particular di- and tri-anisole

and ~~IIIIIII~~ phenetole is dictated by the possibility ~~IIIIIIIIIIIIIIII~~ offered to employ them

to make ammonium nitrate explosives. Di- and trinitrophenols are unsuited to this

purpose, as they react with the nitrate to form nitric acid. The ethers of the

di- and trinitrophenols are less sensitive, but more powerful explosives than

are the responding nitrophenols. Like the ethers, they are capable of undergoing

~~IIIIIIIIIII~~ hydrolysis (even with water) to form the corresponding phenols and

alcohols. ~~IIIIIIII~~ Hydrolysis goes the more easily, the larger the number of nitro

groups in the nitro ether.

The most important of the nitro derivatives of ~~the~~ phenol ethers is ~~IIIIIIIII~~

~~IIIIIIIIIIIIIIIII~~ dinitroanisole $C_6H_3(NO_2)_2OCH_3$, the production of which attained

300 tons per month in Germany in 1944.

Dinitroanisole is a crystalline substance that exists in two modifications,

one of which has a freezing point of 86.9°, and the other 95°. Its **heat** of

formation is **XXXXXX** 46.42 kcal/mole (Bibl.216). Dinitroanisole dissolves in

water with difficulty, **XXXXXX** better in alcohol and ether, and very well in

acetone and benzene. The following are the explosive characteristics of

dinitroanisole. The volume of gaseous products of explosion is 724 ltr/kg, the

204   velocity of detonation is 5620 m/sec, and the fugacity is 245 cc.

Dinitroanisole is produced by the treatment of dinitrochlorobenzene with

caustic soda in the presence of methyl alcohol, in accordance with the reaction:

$$
\underset{NO_2}{\overset{Cl}{\underset{|}{\bigg|}}}NO_2 + CH_3OH + NaOH \rightarrow \underset{NO_2}{\overset{OCH_3}{\underset{|}{\bigg|}}}NO_2 + NaCl + H_2O.
$$
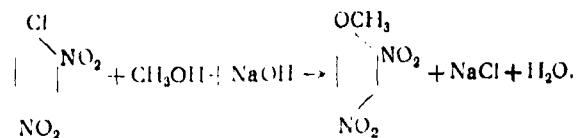
The NaOH solution is added to the mixture of dinitrochlorobenzene and methyl

alcohol at 18 - 20°, with a rise in temperature to 45°. After cooling, the

dinitroanisole is filtered, washed, and dried. The yield is about 94% of

theoretical.

A method of direct nitration of anisole has also been described (Bibl.217).

Dinitroanisole is employed as one of the components in the manufacture of

powders with a non-volatile solvent.

Trinitroanisole: 2,4,6-trinitroanisole $C_6H_2(NO_2)_3OCH_3$ is a crystalline substance

with a melting point of 68.4°. It has somewhat greater brisance than TNT, but **XXXXX**

less than picric acid. The volume of gaseous explosion product is 740 ltr/kg, and

the fugacity is 314 cc.

was
        Trinitroanisole ~~IX~~ produced on a rather large scale ~~IX~~ in Japan during

World War II. It was ~~XXXIX~~ employed in mixtures with RDX (60% trinitroanisole,

40% RDX) and with hexyl (60% ~~XXIXIIXXXXIXXI~~ trinitroanisole, 23% hexyl, and 16%

aluminum). A mixture of 70% trinitroanisole and 30% aluminum was employed in

naval incendiary shells (Bibl.188).

        2,4,6-Trinitrophenetole
        ~~ZYXJXXTXIXIIXXXNXXXIX~~ $C_6H_2(NO_2)_3OC_2H_5$ is a crystalline substance with a

melting point of 81°. The brisance of trinitrophenetole is less than that of

TNT.

        Trinitroanisole and trinitrophenetole are produced by nitrating the

corresponding dinitro derivatives, which in turn, are obtained from ~~IIX~~

dinitrochlorobenzene and the corresponding alcohol, in the presence of caustic

soda (Bibl.218).

        A considerable advantage enjoyed by these ethers over picric acid is their

neutrality, making it possible to employ them in a mixture with ammonium nitrate.

However, ~~it~~ has been pointed out by ~~XXXXXX~~ A.G.Gorst (Bibl.219), the employment of

these mixtures during World War I showed that, in the presence of moisture, the

ethers undergo hydrolysis to convert to picric acid and alcohol.

Section 5. <u>Trinitroresorcinol (Bibl.208, 220)</u>

        Trinitroresorcinol was first obtained in 1808 by Chevreul. In 1946 ~~XXXXXXX~~

                                                      ~~styhnic~~ styphnic
Boettger and Ville again obtained this substance, and called it ~~XXIIXXIX~~ acid.

                                                          styphnic   a
In 1871, Stenhouse and ~~XXXXXXXX~~ Schroeder showed that ~~styphnic~~ acid is ~~XXX~~ product

of the nitration of resorcinol, and has the following formula
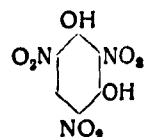
to produce
Trinitroresorcinol is employed/sodium trinitroresorcinate (TNRS), which is

an initiator.

205   Trinitroresorcinol (2,4,6-trinitro-1,3-dioxybenzene) consists of bright

yellow crystals of the hexagonal system. Its specific gravity is 1.83, and

melting point 180°. This product is weakly soluble in water: at 14°, only 0.65%

~~XXXXXXXXXXXXXXXXXXXXXXXXXX~~
dissolves, and at 62°, 1.1%. The solubility in various solvents is shown in

Table 71.

Table 71

a)	b)				
	0	5	10	17	48
Alcohol	5,10	—	—	6,22	14,65
Benzene	—	4,5	—	—	47
Toluene	--	—	5,1	—	—
Acetone	—	—	—	313,1	—

a) Solvent; b) Solubility of trinitroresorcinol, gm, at temperatures,
in °C (in 100 gm solvents)

An aqueous solution of trinitroresorcinol is bright yellow, apparently they
owing to its
~~present its~~ dissociation into ions.

Trinitroresorcinol is a rather strong acid and is similar to trinitrophenol

in its properties. Being a dibasic acid, it can form neutral and acid salts.

Its neutral salts are as stable as the salts of trinitrophenol. A strong aqueous

solution of trinitroresorcinol dissolves iron and zinc to liberate hydrogen, and

this reaction goes with particular ease upon heating. It does react with copper,

sulfur, lead, tin, and cadmium. The carbonates decompose trinitroresorcinol,

with liberation of carbon dioxide.

Nitric and sulfuric acids (dilute and strong) do not react with trinitroresorcinol

even upon boiling, but merely dissolve it. Aqua regia, however, oxidizes it

to oxalic acid and other products. Trinitroresorcinol is somewhat more #######

powerful explosive than picric acid (Bibl.221). Ignited trinitroresorcinol burns

with a bright flame but without explosion. A cap detonator will cause it to explode.

products
Production of trinitroresorcinol. The initial ####### for production of

trinitroresorcinol are resorcinol, nitric acid, and sulfuric or acetic acid.

Resorcinol (meta-dioxybenzene) ####### $C_6H_4(OH)_2$ is a white crystalline

substance. Its specific gravity is 1.272, melting point 110.7^o, and boiling

point 276.5^o.

Table 72 presents the solubility of resorcinol and various solvents.

Table 72

a)	b)				
	0	12	15	24	30
Water	86,4	147	—	—	228
90% Alcohol	—	—	127	—	—
Benzene	—	—	—	2	—

a) Solvent; b) Solubility of resorcinol, gm (in 100 gm solvent) temperature, ^{o}C

Resorcinol is virtually insoluble in chloroform and carbon disulfide. In the

presence of ammonia it takes on a reddish tinge, and in an ammonia solution of

silver nitrate, it ###### reduces silver. With aqueous solutions of ferric chloride,

resorcinol yields a blue color. When chlorine or bromine react with aqueous

solutions of resorcinol, the consequence is trichloro- or tribromoresorcinol. This

is the basis for the method of quantitative determination thereof. To an aqueous

solution of resorcinol, a titrated solution of bromine water is added ###############

204

395

(tribromoresorcinol being obtained), and the excess bromine is determined by

back-titration with iodine and hyposulfite.

Resorcinol does not yield a precipitate ~~with~~ lead acetate, but its ~~XXXXXXXXXXXXXXX~~
~~XXXXXX~~

isomer-pyrocatechinol does form a precipitate.

Resorcinol is obtained from benzene through disulfobenzene as intermediate.

The raw resorcinol is purified by vacuum distillation. Depending upon the degree

of purification, the technical products may contain homologs and isomers as

impurities: phenol, ~~XXXXXXXXXXXXXXX~~ pyrocatechinol, hydroquinone, fluoroglucinol, and ~~XXX~~

diresorcinol. In addition, one also encounters thioresorcinol, organic acids

(salicylic
~~XXXXXXXXXX~~ and phthalic), resins, and water-insoluble impurities. Resorcinol that

has been inadequately purified is ~~XXXX~~ brown in color and smells of phenol. Even

after careful purification by volitilization, steam distillation, and crystallization,

technical resorcinol may still contain phenol and pyrocatechinol.

When technical resorcinol is to be nitrated, the presence of ~~XXXXXXXXX~~ resinous

substances, which cause the nitro mixture to foam up (due to oxidation) and reduce

the quality of the nitro product, is particularly undesirable. Therefore, special

technical requirements must be met by resorcinol, under which its melting point

has to be in the $109 - 111^{\circ}$ interval, the resorcinol content must be not less

than 99%, that of ~~pyrocatechinol~~ pyrocatechinol not over 0.3%, that of phenol and other brominators

must be not more than 0.1%.

Nitration of resorcinol, as that of phenol, can only be performed at low

temperature $(0 - 5^{\circ})$, and by a weak mixed acid or nitric acid. However, ~~XX~~ even

if these conditions are adhered to, the yield of nitro product is small because

of oxidation.

Considerably smaller losses of resorcinol due to oxidation occur when it is nitrated by a diacetyl derivative. To do this, a finely ground resorcinol is dissolved in glacial acetic acid or in acetic acid chloroanhydride. The result of the reaction is formation of a diacetyl resorcinol solution, which is ~~XXXXXX~~ run into ~~XXX~~ strong ~~XXXXXX~~ nitric acid, accompanied by careful agitation and cooling. Three times the theoretical quantity of nitric acid is employed. After run-in, the reaction mixture is permitted to stand for 3 or 4 hrs, with continued stirring, and with heating from time to time until bubbles begin to be emitted. At the end of the holding time, the mass is poured into five times the quantity of commercial sulfuric acid, with cooling and agitation, and is heated to 60° for 2 hrs. The resultant reddish brown mass is poured into a large amount of water, in which the bright yellow crystals of trinitroresorcinol come down. The product yield is approximately 70% of theoretical.

Today, trinitroresorcinol is obtained through resorcinol sulfonic acid as intermediate, with subsequent nitration of the final product. The yield is 84% of theoretical. The technology is substantially similar to that of the production of picric acid, and consists of the following.

Resorcinol is finely ground in iron drums with cast-iron balls, or on special mills. Commercial ~~XXX~~ sulfuric acid is run from the metering tank into the sulfurate, and the resorcinol is run in batchwise, with the agitator operating. The sulfuric acid has to be five ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX~~ times the theoretical, by weight, in order for disulforesorcinol to be formed. Sulfonation is performed at 35°, and, at the end

of the process, result is a reddish-violet transparent solution of disulforesorcinol in sulfuric acid. In order to bring the reaction all the way to completion, the sulfo mixture is held for 1 - 1.5 hrs at 60 - 70°, subsequent to which the disulforesorcinol solution is cooled to 30°, and nitration is undertaken.

Therefore, mixed acid is gradually run into the disulforesorcinol in sulfuric acid solution, thus raising the temperature to 37°. At the conclusion of the run-in, formation of trinitroresorcinol crystals begins, as a consequence of which the viscosity of the mass increases, and liberation of nitrogen oxides

207   results in foam formation. ꜰꜱꜱ If stirring is inadequate, due to foaming, the ꜱꜱꜱꜱ consequence may be local overheating and sudden changes in temperature. Therefore, particularly careful stirring is necessary at this stage in the process. To do this, a foam-breaker is provided on the agitator. Should there be a sudden jump in temperature, the nitro mixture has to be dumped into the emergency pot. At the conclusion of the run-in, the temperature is raised to 50°, and is then held for an hour at 60 - 65°. Completion of holding is determined by the color of the crystals, which have to be from orange ꜱꜱꜱ to yellow. The nitro mass is then cooled to 25 - 35°, and drained into a dilution tank filled with water. This operation is accompanied by foaming and increase in temperature, and therefore has to be performed stepwise, to avoid sudden emission of nitrogen oxides and sudden changes in temperature.

Upon dilution, trinitroresorcinol comes down as a precipitate, inasmuch as its solubility in the water is less than in spent acid. The crystals are separated from spent acid in a vacuum funnel, and are washed first with ꜱꜱꜱꜱ warm water (50°), and then with cold (20°).

398

When low-grade ~~HHHIXX~~ resorcinol are employed, the trinitroresorcinol is

purified by treatment with sodium bicarbonate:

$$C_6H(NO_2)_3(OH)_2 + 2NaHCO_3 \rightarrow C_6H(NO_2)_3(ONa)_2 + 2CO_2 + 2H_2O.$$

Neutralization of sulfuric acid to Na_2SO_4 occurs simultaneous with the ~~XX~~

above reaction. Further treatment of the solution obtained by nitric acid results

is
in precipitation of pure nitroresorcinol. About 5% of the product/lost in

purification. Purification is performed as follows.

3 - 4 times
The trinitroresorcinol is mixed with ~~XXXXXXXXXXXXXXXXXXXXX~~ its weight in water,

and a ~~XX~~ 12.5% sodium bicarbonate solution, in a little more than the theoretical

quantity, is ~~XXXXXX~~ run into this mixture in a thin stream at $85 - 90^o$. The

approximately 15% sodium trinitroresorcinol solution obtained is cooled to

$40 - 45^o$ and treated with strong nitric acid. The precipitated trinitroresorcinol

is refiltered and washed with water. The product yield is about 78% of the

theoretical. After purification, it is dried in a rack-type drier at $50 - 60^o$,

for 36 hrs.

The technical product usually contains isomers, mono- and di-nitroresorcinol,

as well as a certain amount of H_2SO_4. The trinitroresorcinol employed to produce

lead trinitroresorcinate has to ~~XXXXXX~~ satisfy the following conditions: melting

point not under 174°, water-insoluble impurities not over 0.5%, ashes not over 1%,

and H_2SO_4 not over 0.2%.

Section 6. Trinitrocresol and Other Nitro Derivatives of Cresol

Trinitrocresol can only be regarded as an auxiliary explosive to be obtained

from an extra source of raw material - cresol. It has no particular advantages as

~~XXXXX~~

399

an explosive over picric acid, if we do ₦X not consider its lesser degree of

solubility in water and lesser reactivity. It is equal to TNT in its explosive

qualities.

The starting material – cresol – is hardly suited to nitration in the raw

form, as it consists of a mixture of meta-, ortho-, and para-isomers, of which only

the meta-cresol yields a ~~XXIXIXXXXXXXIXXIXX~~ trinitro derivative.

208   Trinitro-meta-cresol is a bright yellow crystalline substance melting at

109.5°. Its formula is
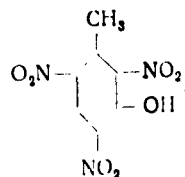
A trinitro-meta-cresol of 1.64 density may be produced by pressing and

pouring. It dissolves in water less readily than does ~~XXXXX~~ picric acid. Thus,

100 parts water by weight will dissolve (in parts by weight)

```
at  6°  . . . . . . . . . . .  0,15
at  25° . . . . . . . . . . .  0,20
at  100° . . . . . . . . . .  1,83
```

Trinitro-meta-cresol readily dissolves in alcohol, ~~XXXXXXX~~ ether, benzene,

and acetone. Its chemical properties are similar to those of picric acid. With

         salt^s, so-called
metals and oxides thereof, it forms ~~XXXXXXXX~~ cresylates. Cresylates are somewhat

less sensitive to shock and heating than ~~XXXX~~ are the corresponding picrates. Like

the picrates, the most sensitive are the salts of the heavy metals, and the most

sensitive of all is the lead salt.

Trinitrocresol is a wholly stable substance, which begins to decompose

at about 200°. Its flash point is 2°5°. It is somewhat less shock-sensitive

than picric acid, and is inferior thereto in fugacity and braisance. Trauzl bomb

expansion is 290 cc, braisance, according to Kast is 2X 4.2 mm, velocity of

detonation is 6850 m/sec, volume of gaseous explosion product is 675 ltr/kg, and

heat of explosion is 912 kcal/kg.

Trinitrocresol is not employed by itself. In France, it has been employed
in
XXXX alloys with picric acid. The most frequently used was an alloy of 60%

trinitrocresol 40% picric acid, called cresolite. A valuable property of this
it
alloy is the fact that XX is less sensitive than picric acid, has a low melting

point (75 - 80°) and is plastic at 65 - 70°, which makes it possible easily to

obtain a dense charge (Δ = 1.65). In Austria, employment was made of an

ammonium salt nitrocresol, which has no particular value as an explosive.

Production of trinitrocresol. The starting material for production of

trinitrocresol is meta-cresol which is obtained from the neutral oil of coal tar,

in a mixture with ortho- and para-cresol. Technical coal cresol is of approximately

the following composition: 40% ortho-, 35% meta- and 25% para-isomer. Table 73

presents the properties of cresol isomers.

Table 73

a)	b)	c)
Ortho-	190,8	30
Meta-	202,8	3—4
Para-	202,0	36

a) Cresol isomer; b) Boiling point, °C;
c) Melting point, °C

Upon nitration,
XXXXXXXXX meta-cresol yields

2,4,6-trinitro-meta-cresol, with a yield

of about 80%. Under the conditions of

nitration of the meta-isomer, the XXX

ortho- and para-cresols undergo complete

oxidation with formation of oxalic acid.

Nitration thereof at low temperature makes it possible to obtain the

trinitro derivatives, which are, however, so unstable as to decompose even under

the effect of cold water. Therefore, before technical cresol may be used for

nitration, it is distilled, to separate the ortho-isomer, the para- and

meta-isomer remaining in the mixture, inasmuch as their boiling points are quite

similar. The so-called technical meta-cresol, thus liberated, contains about

40% para-cresol.

Further separation of these isomers may be achieved by ~~XX~~ oleum treatment of

technical meta-cresol. The result is that the para-cresol goes into a crystalline

sulfo compound, poorly soluble in acid, and the meta-cresol goes into a sulfo

compound readily soluble in acid. The crystals of the para-cresol sulfo compound

are filtered off, and the solution of the sulfo compound of ~~XXXXXXXXXX~~ meta-cresol

in sulfuric acid ~~XXXXXX~~ are nitrated, to yield trinitro-meta-cresol.

Nitration may be employed to obtain the dinitro derivative from the sulfur

derivative of para-cresol, or , by live-steam treatment, to recover the initial

para-cresol.   However, it is more economical to use techńical meta-cresol in nitration,

without ~~XXX~~ separating the para-isomer.

The technical process of production of trinitrocresol is similar to that involved

in obtaining nitric acid from phenol. The yield of trinitrocresol is about 50% of

the theoretical. This low yield is explained by the oxidation of para-cresol.

In recent years, considerable interest has developed in 3,5-dinitro-ortho-cresol

CH_3

—OH

O_2N NO_2

402
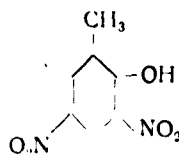
as a product of considerable herbicidal activity. This product may be produced may

via the disulfo derivative of ortho-cresol, for example, by saturating it with an

aqueous solution of nitrogen oxides (Bibl.222).

Not long ago, a patent has been published (Bibl.223) for a continuous method of

producing dinitro-ortho-cresol, in accordance with which 12.9 kg ortho-cresol and

34 kg 70% nitric acid are admitted, in the course of an hour, through a calibrated

nozzle, into a water-cooled metallic tube 1 m long and 38 mm in diameter. The yield

of dinitro-ortho-cresol was 80% of the theoretical.

CHAPTER VI

NITRO COMPOUNDS OF THE ALIPHATIC SERIES

A. General Description

The nitro compounds of the aliphatic series XXX(nitro paraffins, nitro alkanes) have come into wide use in the last 10 - 15 years as components of jet fuels. Because of their high reactivity, they may be employed as the starting materials for the production of XXXX a number of valuable chemicals, acids, amines, nitroalcohols, etc., as well as for the synthesis of powerful explosives. The problem of obtaining and utilizing nitro compounds of the aliphatic series XX for these purposes is also XXXX important because a cheap and large supply of raw materials for them is available, inasmuch as XX paraffins are XXXX a basic component of petroleum, industrial, and natural gas.

210 The nitroalkanes were XXX obtained in 1872 by V.Meyer by reacting silver nitrite with alkyl iodides:

$$C_nH_{(2n+1)}J + AgNO_2 \rightarrow C_nH_{(2n+1)}NO_2 + AgJ.$$

Subsequently, this reaction came to be performed by XX reacting·nitrite salts other metals with sulfuric esters, for example:

$$\begin{array}{c} CH_3O \\ \diagdown \\ CH_3O \diagup \end{array} SO_2 + I'NO_2 \rightarrow CH_3 - NO_2 + CH_3OSO_2OK.$$
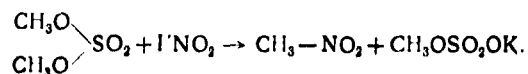
The reaction product included not only nitro compounds, but nitric esters (for example, XX CH_3ONO), and, because of their lower boiling point, these latter XXXX were readily separable from the basic product by distillation.

Formation of nitro compounds as a result of the reaction of nitrite having a tri-valent nitrogen atom, XX is explained by the fact that, along with the exchange reaction, leading to the formation of nitric esters, there is a halide alkyl

addition reaction, K followed by the cleaving off of a halide salt:

$$Ag^{\oplus}[\overset{\ominus}{O}-N--O] + CH_3-J \rightarrow \left[Ag-O-\overset{\cdot\beta}{N}\overset{O}{\underset{CH_3}{\diagup}}\right]J^{\oplus} \rightarrow$$

$$-\cdot AgJ + O^{\ominus}-N\overset{O}{\underset{CH_3}{\diagup}} \left(or \quad O \leftarrow N\overset{O}{\underset{CH_3}{\diagdown}} \right).$$
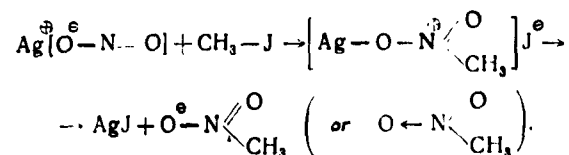
The obtaining of nitroalkanes by means of $AgNO_2$ is of significance only in the laboratory. Running this reaction in XXXIMMMIXXXXXIX dimethylsulfoxide or dimethylformide, containing urea, makes it possible to XXXMMIXXX employ $NaNO_2$ instead of $AgNO_2$. When this is done, the yield of primary and secondary nitroalkanes attain 60% (Bibl.1, 2).

Twenty years later, in 1892, M.I.Konovalov obtained nitroparaffins by direct reaction of nitric acid (10 – 15% strength) upon liquid saturated hydrocarbons: pentane, hexane, etc., at temperatures in the vicinity of 115 – 150°. Considerably later, A.I.Titov, investigating this reaction, demonstrated, (Bibl.3), that the active XXIXI chemical agent therein is a molecule of the monomer of nitrogen dioxide, similar to a radical, and XXXXXIXXXX regenerated from nitric acid.

Reaction of the nitrogen dioxide monomer with paraffin hydrocarbons results in the formation of radicals

$$R:H + \cdot NO_2 \rightarrow R\cdot + HNO_2,$$
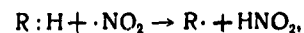
which combine with extreme rapidity with the next molecule of the nitrogen dioxide monomer

$$R\cdot + \cdot NO_2 \rightarrow R-NO_2.$$
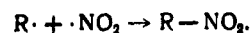
Simultaneously, the regeneration of $\cdot NO_2$ occurs

$$HNO_2 + HNO_3 \rightarrow H_2O + 2\cdot NO_2.$$
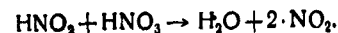
Formation of nitric esters is also possible as side products:

$$\cdot NO_2 \rightarrow \cdot O - NO;$$
$$R \cdot + \cdot O - NO \rightarrow R - ONO.$$
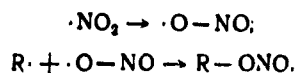
211   These latter go into a series of reactions, reversible in nature, such as

hydrolysis

$$R - ONO + H_2O \rightleftharpoons ROH + HONO$$
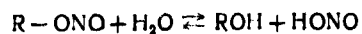
and other transformations.

To be noted that the ease with which substitution by the nitro group occurs

increases as one proceeds from the primary hydrogen (in the CH_3 group) to the secondary

(in the $=CH_2$ group). The substitution of the ternary hydrogen goes easiest of all

(in the group $\equiv CH$).

When nitric acid is reacted with paraffin hydrocarbons, oxidation products (Bibl.4)

are produced in significant quantity simultaneous with the nitration product. The

yield of these oxidation products not infrequently exceeds the yield of the nitro

compounds, particularly if the process is run at high temperature, inasmuch as the

temperature coefficient of the oxidation reaction is higher than that of the nitration

reaction.

It is proposed that nitrogen dioxide be employed to XIXXXX nitrate paraffin

hydrocarbons instead of nitric XXIXXX acid. This process is run in liquid phase at

150 - 200° at 20 atm pressure (Bibl.5,6).

A.I.Titov expresses the mechanism of formation of oxidation products in the

nitration of paraffin hydrocarbons as follows (Bibl.3):

XXXXXXXXXXX
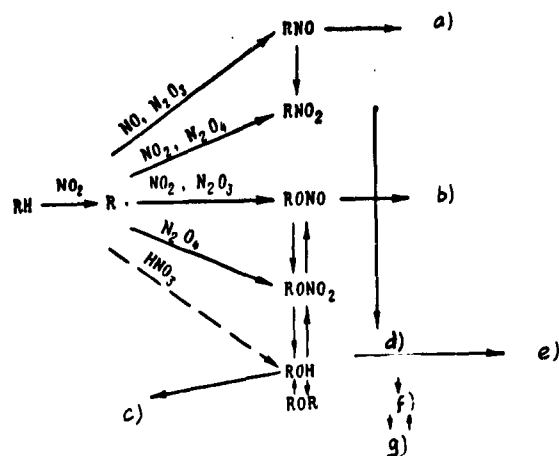
a) Oxines and other conversion products; XXXX b) Lower radicals, ketones,
aldehydes, and their conversion products; c) Olefines and their conversion
products; d) Ketones, aldehydes; XXX e) Lower acids, nitriles, HCN, oxy acids, etc.;
f) Acids; g) Esters

Nitration of paraffin hydrocarbons in the liquid XXX phase is rendered difficult
by the fact that the hydrocarbons and the nitric acid are mutually insoluble, and,
moreover, the resultant nitro product is partially soluble in nitric acid, with the
consequence that it undergoes further nitration and oxidation.

In 1936 and 1937, studies appeared on the nitration of pentanes and butanes in
the gaseous phase by nitric acid of 1.5 specific gravity. According to the data
of Rachman (Pibl.7,8,9), this process goes better in the presence of halides or
oxygen, which facilitate the formation of low-molecular nitro paraffins. The
mechanism by which these additives XXXXXXXX operate consists of the formation of
free hydrocarbon radicals arising through the reaction of the hydrocarbon with the
halide or oxygen. Moreover, the halides take up the nitrogen oxide, and prevent
nitration.

XXXXX

211   In the gaseous phase, the reactants are miscible in any proportion. The essence

of the product lies in the fact that the hydrocarbon vapors are passed through a

coil reactor, into which hot, strong nitric acid is admitted simultaneously. Passed

the coil reactor, the mixture of hydrocarbon and nitric acid fumes passes through a

212   reaction apparatus in which a temperature of $400 - 450°$ is maintained. As a

consequence, the free radicals formed at high temperature (Bibl.9) participate in the

reaction. Thus, when the first law a process of decomposition of paraffin hydrocarbons

into free radicals: $R - R$ $2R\cdot$, and then subsequent combination thereof with a

decomposition product of nitric acid: NO, NO_2, H_2O, into nitroso-, nitro-, and

oxyparaffins.

At a temperature of $400 - 450°$, derivatives of the lower hydrocarbons are obtained

from the higher paraffin- hydrocarbons. However, if the process be run at

a temperature under $350°$, cracking of the paraffins does not occur, and formation

of products of nitration and oxidation of the hydrocarbons taken for nitration occurs.

For the explosives industry, it is only the nitro derivatives of the lower

hydrocarbon paraffins that are of interest: nitromethane and nitroethane. The latter

vapor-phase
may be obtained by nitration at $400 - 450°$, from the higher paraffinic

hydrocarbons, constituting a component of petroleum (Bibl.10, 11). The ratio of the

components is of importance in connection with process safety. When the HNO_3-to-

hydrocarbon ratio is 8:1, one obtains a stoichiometric ratio of combustible and

oxidizer, constituting and explosive mixture. Therefore, the process is run with

mixtures containing excess hydrocarbon (from 2.5 to 10 parts by weight per part HNO_3

by weight).--This simultaneously facilitates an increase in the yield of nitration

products.

In nitration in the vapor phase, more than 60% of HNO_3 is consumed in oxidizing

processes, in which it is reduced to nitrogen oxides. The nitrogen oxides are sent

to absorbers to recover nitric acid. This significantly reduces the dead losses

thereof, and the degree of loss is governed solely by the completeness of which the

apparatus is sealed.

The resultant nitroparaffins must immediately be removed from the high-temperature

zone, and cooled, to prevent decomposition thereof. The temperature and time of

contact of hydrocarbons with HNO_3 are interdependent. The higher the temperature,

the less must be the contact time. For example, for pentane at 450°, 0.22 sec contact

time is adequate, at 398°, 1.0 sec. will do, and 366° – 2.9 sec, and at 248° – 852 sec.

The optimum temperature for the various hydrocarbons differs and is determined by

their stability. The more difficult it is for a hydrocarbon to be cracked, the higher

must be the temperature of nitration in the vapor phase. Thus, for example, the

optimum nitration temperature of methane is $550 - 600^{\circ}$, that of ethane is $500 - 550^{\circ}$,

propane – $410 - 450^{\circ}$. butane – $380 - 410^{\circ}$.

The optimum temperature drops with increase in the molecular weight of the

hydrocarbon, and with branching of the carbon chain. Hydrocarbons of larger molecular

weight and, molecular weight being equal, isomeric hydrocarbons, crack more

readily. Pressure, which does not affect the nature of vapor-phase nitration, has

a major effect upon its velocity, inasmuch as an increase in pressure is accompanied

by an increase in the volumetric concentration of the components. This makes it

possible to reduce the contact temperature and time. Nitration is usually performed

at 7 – 10 atm. There are also installations that function at atmospheric pressure.

Installations functioning under pressure are more compact, and the reaction goes

212   at lower temperature, however this requires absolute airtightness of apparatus ~~(XXXXXXX)~~ the

(Bibl.5,10).

The iron walls of the apparatus are inhibitors of vapor-phase nitration and

sharply diminish the yield of nitroparaffins. The introduction of KNO_3 or $NaNO_3$ ~~XXXXX~~

into the apparatus makes it possible to reduce this effect somewhat (Bibl.9).

In the USA, ~~gas~~-phase nitration is performed in reactors of chrome-nickel steel.

The metering and delivery of the components is automatic. They are preheated by ~~XXXXXX~~ passive

213   ~~XXXXXX~~ ~~transmission~~ through heat exchanges or tubular furnaces. The ~~duration of the~~ residence time

~~stay~~ of the mixture in the reactor is regulated by the rate of component delivery.

mixture
The ~~XXXXXX~~ goes from the reactor to a condenser. The distance between reactor

and condenser should be minimal so as to assure rapid cooling of the nitroparaffins

and prevent decomposition thereof. Cooling is performed stepwise. High-boiling

fractions condense in one condenser, and low-boiling in another. These fractions go

to preliminary distillation, subsequent to which each fraction is subjected to chemical

purification and is again distilled in a/distillation apparatus.
                                               fractional

Figure 64 shows a schematic diagram of the apparatus for gas-phase nitration.
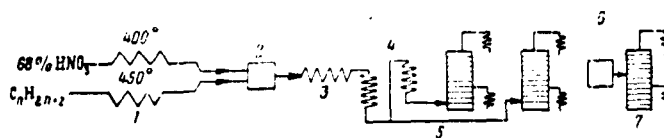
Fig.64 - Diagram of Apparatus for Gas-Phase Nitration of Aliphatic Hydrocarbons

1 - Heater; 2 - Mixer; 3 - Reactor; 4 - Condenser; 5 - Preliminary distillation;

6 - Chemical purification; 7 - Distillation

In some apparatus, the nitric acid is not heated to high temperature (of the order

of 250 - 400°) but is merely vaporized. This prevents deep decomposition to NO and O_2.

A number of indirect methods of producing nitroparaffins (Bibl.12,13,14) are

also known:

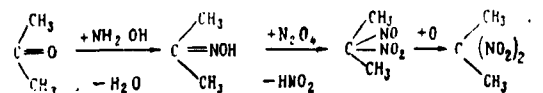1) oxidation of amines in accordance with the following mechanism

$$2RCH_2NH_2 \xrightarrow{O_2} 2RCH_2NHOH \xrightarrow[-2H_2O]{O_2} 2RCH\!-\!NOH \xrightarrow{O_2} 2RCH_2NO_2.$$
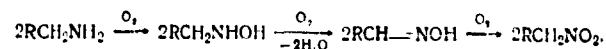
The yield of nitroparaffins is 30 - 50%. Nitrocompounds are formed upon the

the
oxidation of the primary amines only. Oxidation XX does not cause/secondary and

ternary amines to yield nitro derivatives. Reaction of olefins with nitrogen

tetroxide goes as follows:

$$2\,(CH_3)_2C\quad C\,(CH_3)_2 + 2N_2O_4 < \begin{array}{l} {}^{(CH_3)_2\,C\,(NO_2) - C\,(NO_2)\,(CH_3)_2}\\ {}^{\cdot(CH_3)_2\,C\,(ONO) - C\,(NO_2)\,(CH_3)_2} \end{array}$$
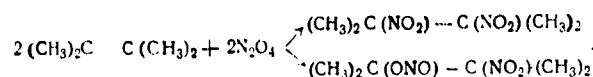
The dinitro compound constitutes 30 - 50% of the mixture, while the residue

consists of nitroalkyl nitrite. This latter has a ten.ency to spontaneous decomposition,

which is responsible for the instability of the resultant reaction mixture;

2) reaction of ketones with nitric esters (Bibl.15) or with hydroxyl amine,

followed by reacting nitrogen and an oxidizer (a chromium mixture or nitric acid)

with resultant oxime in accordance with the following mechanism

$$\underset{CH_3}{\overset{CH_3}{C}}\!=\!O \xrightarrow[-H_2O]{+NH_2\,OH} \underset{CH_3}{\overset{CH_3}{C}}\!=\!NOH \xrightarrow[-HNO_2]{+N_2O_4} \underset{CH_3}{\overset{CH_3}{C}}\!\!\overset{NO}{\underset{NO_2}{-}}\ \xrightarrow{+O} \underset{CH_3}{\overset{CH_3}{C}}\!(NO_2)_2$$

The yield of dinitro compound is 25 - 35%;

3) permanganate oxidation of ternary carbinamines is employed to obtain ternary

nitro compounds, the yield being 70 - 80% ('Bibl.16).

Properties of nitroparaffins (Bibl.17). Mononitroparaffins are colorless liquid

Table 74 shows the physical properties of mononitroparaffins, from which it is

clear that, as the molecular weight XXXXXXXXX of mononitroparaffins rises, their

boiling point increases, and their specific gravity diminishes.

Mononitroparaffins are poorly soluble in water. Thus, 10.5 cc nitromethane

dissolves in 100 cc water at 100°. The solubility of the residual members of the

214   homologous XX series diminishes as molecular weight rises. The mononitroparaffins

are readily soluble in benzene, toluene, xylene, alcohol, acetone, and carbonic acid.

The lower nitroparaffins are themselves solvents for many organic substances.

Table 74

a)	b)	c)	d)	e)
Nitromethane	CH_3-NO_2	101,2	1,132	1,3935 (at 20°)
Nitroethane	$CH_3-CH_2-NO_2$	114,0	1,047	1,3901 (at 24°)
1-Nitropropane	$CH_3-CH_2-CH_2-NO_2$	131,6	1,008	1,4003 (at 24°)
2-Nitropropane	$CH_3-CH-CH_3$ NO_2	120,8	1,024	—
1-Nitrobutane	$CH_3-(CH_2)_2CH_2NO_2$	152,9	—	—
2-Nitrobutane	$CH_3-CH_2-CH-CH_3$ NO_2 .	139,6	0,988	—
1-Nitro-2-methylpropane	$\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CH-CH_2-NO_2$	137—140	—	—
2-Nitro-2-methylpropane	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	126,5	—	—
1-Nitropentane	$CH_3-(CH_2)_3-CH_2-NO_2$	172—173	0,948	1,4218 (at 20°)
1-Nitrohexane	$CH_3-(CH_2)_4-CH_2-NO_2$	193—194	0,949	—

a) Compound; b) Formula; c) Boiling point, °C; d) Specific gravity at 15°;

e) Refractive index

Dinitroparaffins are XXX colorless, and in a majority of cases crystalline

substances, insoluble in water, and readily soluble in organic solvents.

In the primary and secondary nitro compounds, the hydrogen, standing near the

carbon, bound to the nitro group, is mobile, and therefore these nitro compounds are

capable of undergoing a number of reactions characteristic thereof. They react with

aqueous solutions of caustic alkalis, forming water-soluble compounds with the

properties of neutral salts. These substances are XXX salts of the isonitro compounds,

and constitute strong acids.

Reaction of nitro compounds with alkalis follows this mechanism:

$$CH_3—CH—N^{\oplus}\underset{O}{\overset{\!\!/\!\!O}{\diagdown}}_\ominus + Na^{\oplus} \rightarrow \left[CH_3—CH=N^{\oplus}\overset{O^\ominus}{\underset{O^\ominus}{\diagdown}}\right]Na^{\oplus} + H_2O.$$
$$\underset{I}{}\quad\underset{H+OH^\ominus}{}\qquad\qquad\qquad \underset{II}{}$$
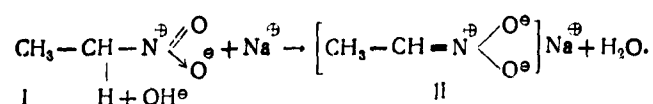
215 The fact that the neutral nitro compounds are isomerized to acid isonitro compounds

is confirmed by the fact that when strong acid reacts with an isonitro compound salt

(II) the water-insoluble nitro compound (I) is not obtained immediately. First, the

XXXXIIXXXXIXXXXXIXKIX isonitro compound (III), which is readily soluble in water, is

liberated, and it undergoes conversion to nitro compound (I) only gradually:

$$\left[CH_3—CH—N^{\oplus}\overset{O^\ominus}{\underset{O^\ominus}{\diagdown}}\right]Na^{\oplus} \xrightarrow[-NaCl]{HCl} \left[CH_3—CH=N^{\oplus}\overset{O^\ominus}{\underset{O\bullet}{\diagdown}}\right]H^{\oplus} \rightarrow$$
$$\underset{II}{}\qquad\qquad\qquad\qquad\underset{III}{}$$
$$\rightarrow CH_3—CH_2—N^{\oplus}\overset{\!\!/\!\!O}{\underset{O^\ominus}{\diagdown}}.$$
$$\underset{I}{}$$
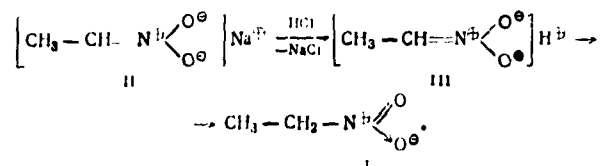
                                    isolate
It has not been possible to XXXXXXX the simplest isonitro compounds in the pure

form, because their conversion into true nitro compounds occurs very rapidly.

It is possible to replace one hydrogen atom in the secondary nitro compounds, and

one or two hydrogen atoms in the primary nitro compounds by halide atoms, as a

consequence of reacting halogens with alkaline solutions of the nitro compounds. This

results in the following compounds:

$$R-CHBr-NO_2; \quad R-CBr_2-NO_2; \quad \underset{R'}{\overset{R}{>}}CBr-NO_2.$$
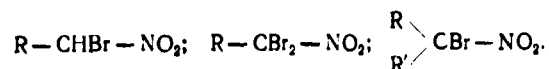
The reaction with nitrous acid is characteristic and permits differentiation of

the primary, secondary and ternary nitro compounds:

a) the primary nitro compounds react with nitrous acid to form so-called nitrolic

acids:

$$R \cdot CH_2 - NO_2 + ON - OH \rightarrow R - C \underset{NO_2}{\overset{NOH}{<}} + H_2O.$$
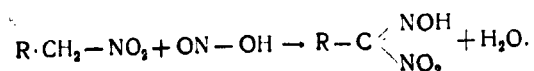
The alkaline salts of nitrolic acids are bright red;

b) the secondary nitro compounds react with nitrous acid to form so-called

pseudonitrols:

$$\underset{R'}{\overset{R}{>}}CH-NO_2 + HO-NO \rightarrow \underset{R'}{\overset{R}{>}}C\underset{NO_2}{\overset{NO}{<}} + H_2O.$$
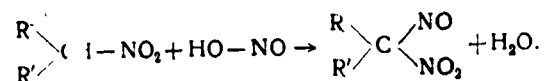
In the crystalline state, these substances are colorless, but in the fused

condition and in solutions (in ether, chloroform, etc.) they have a bright turquoise

coloration;

c) the ternary nitro compounds do not react with nitrous acid.

Reduction of the nitro compounds results in the formation of the primary amines:

$$CH_3 - NO_2 + 6H \rightarrow CH_3 - NH_2 + 2H_2O.$$
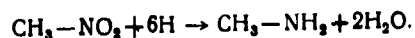
This reaction shows that in nitro compounds, the nitrogen atom is directly bound

to the carbon atom. On the contrary, in reduction of isomeric nitro compounds of

nitrous esters, in which an alkyl is bound to oxygen, one obtains alcohol or ammonia

215 or hydroxylamine:

$$CH_3 - O - N \!=\! O + 4H \rightarrow CH_3OH + NH_2OH.$$
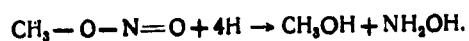
The products of reduction of nitro compounds in an alkaline medium are

aldoximes and ketoximes. It is probable that the isonitro compound is reduced in

these cases: ...

$$R \cdot CH - NO - OH + 2H \rightarrow R - CH \!=\! N - OH + H_2O.$$
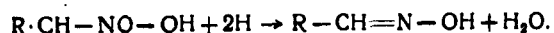
Under conditions of reduction by tin and hydrochloric acid, oximes are capable

of being hydrolized, and decompose to form hydroxylamines and aldehydes or ketones.

216 The primary and secondary nitro compounds enter into condensation reactions with

the aldehydes under the influence of alkalis, to yield nitro alcohols (Bibl.18),

for example:

$$R - CH - O + CH_3 - NO_2 \rightarrow R - CH\,(OH) - CH_2 - NO_2.$$
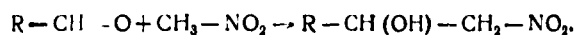
Under specific conditions (acid reactions), the nitro alcohol obtained may be

converted to a nitro olefine;

$$R - CH \!=\! CHNO_2.$$
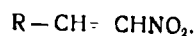
Primary nitroparaffins condense more readily than secondary.

B. Major Nitroparaffins.

Section 1. Nitromethane

Nitromethane CH_3NO_2 has recently found application in a number of countries as

a rocket-fuel component and as an additive to diesel fuel. Its use has been

suggested as a solvent for cellulose nitrates and as an explosive in explosive

drilling operations in petroleum recovery It may be employed as a starting product

to produce chloropicrin (CCl_3NO_2), tetranitromethane, and a number of

explosives.

Nitromethane is XXX a colorless liquid, boiling point 101°, freezing point -29°

(Bibl.19, 20). Table 75 illustrates the specific gravity and viscosity of nitromethane

at various temperatures.

The thermal capacity of nitromethane at 20C

is c_p = 2.07 cal/mole/°C.

Nitromethane is soluble in water (about 9%,

at 20°), and itself dissolves 2.2% water. It is

miscible with virtually all organic liquids, and

is a good solvent for many organic and inorganic

substances, including cellulose esters and certain

resins.

Table 75

a)	b)	c)
10	1,1490	0,748
25	1,1287	0,625
40	1,1080	0,533

a) Temperature, °C; b) Density,
gm/cm^3; c) Ostwald viscosity

Nitromethane is a reactive substance. Caustic alkalis induce a peculiar

condensation of two molecules thereof, leading to the formation of methazonic acid:

$$2CH_3NO_2 + 2KOH \rightarrow \underset{KO}{\overset{O}{>}} N=CH-CH=NOK + 3H_2O.$$
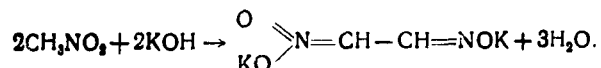
Nitromethane and excess formaldehyde forms triatomic alcohol:

$$3CH_2O + CH_3-NO_2 \rightarrow (HC-CH_2)_3C-NO_2.$$
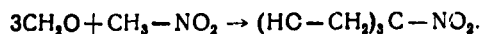
Upon esterification by nitric acid, this alcohol will, like glycerol, yield a

trinitrate $(O_2N - O - CH_2)_3C - NO_2$ - which is a very powerful explosive.

Nitromethane is an explosive having a negative oxygen balance. Its brisance,

according to Hess, is 25 mm(with an auxiliary TNT cap of 5 - 8 gm). The fugacity in

the Trauzl block is 470 cc. Shock sensitivity is as follows: the dropping of a 10 kg

weight from a height of 25 cm yields 0 - 8% explosion. Velocity of detonation is

6600 m/sec (Bibl.21).

Nitromethane is a toxic substance (Bibl.22).

Nitromethane is obtained on an industrial scale in *gas*-phase nitration of

paraffin hydrocarbons, and also by a number of indirect methods (Bibl.23, 24). Direct

nitration

~~MMMMXXX~~ of methane has not yet been performed on an industrial scale. Nitration of

provides
methane by nitric acid in the gas phase under laboratory conditions ~~MMMMM~~ a nitromethane

yield of about 25%.

Of the method of producing nitroparaffins described above, the method involving

the production of nitromethane from dimethylsulfate is of practical significance:

$$O_2S\begin{array}{c} \diagup OCH_3 \\ \diagdown OCH_3 \end{array} + 2NaNO_2 \rightarrow 2CH_3-NO_2 + Na_2SO_4.$$
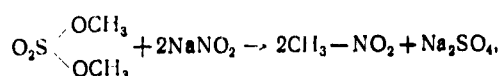
which gives
~~XMMMXXXMMM~~ a yield of about 60%. The reaction is run in an aqueous solution, first

at 60°, and then at 120°, in the presence of small amounts of K_2CO_3 (Bibl.25).

Nitromethane may also be obtained by reacting chloroacetic acid with potassium

nitrite or sodium nitrite in aqueous solution. The nitroacetic acid ~~IMX~~ resulting

therefrom decomposes upon boiling with water:

$$CH_2Cl-COOH + NaNO_2 \rightarrow \underset{\underset{NO_2}{|}}{CH_2-COOH} \rightarrow CH_3NO_2 + CO_2.$$
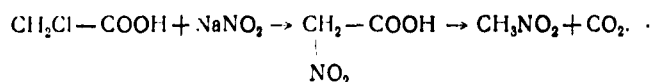
Section 2. Dinitromethane

Dinitromethane $CH_2(NO_2)_2$ was first obtained in 1893 by Duden (Bibl.26). Thanks

to its exceedingly high reactivity and the presence of two mobile hydrogen atoms, it

is able to serve as the basis for the production of polynitro compounds. ~~IIMMMM~~

Dinitromethane is a colorless, free-flowing and volatile liquid with a characteristic

sharp odor, recalling that of methanoic acid. It is stable only at low temperature,

whereas at room temperature it decomposes within a few minutes to liberate nitrogen

oxide (Bibl.26).

Dinitromethane may be driven over without decomposition only with benzene vapors.

It is virtually ▨▨▨▨ insoluble in cold water but rather soluble in warm water (Bibl.28).

Ether and benzene solutions are stable and may be stored for a long time (Bibl.26).

Studies of the absorption spectra (Bibl.29, 30) and ▨XX▨▨▨ the electrical ▨▨▨X

conductivity of aqueous solutions (Bibl.27) have shown that dinitromethane may exist

in two tautomeric forms:

$$CH_2(NO_2)_2 \rightleftarrows NO_2CH=NOOH.$$
$$\text{I} \qquad\qquad \text{II}$$
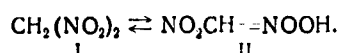
Free colorless dinitromethane is a true nitro compound (I). In anhydrous

unpolarized organic solvents (benzene, ether), dinitromethane also exists in the form

of a true nitro compound, in which case the solutions are colorless.

Dinitromethane has a tendency to convert to the acy form (II), solutions of which

are yellow. Conversion of dinitromethane goes more rapidly when water is added. In

aqueous solution, ▨▨ dinitromethane is a monobasic acid, similar in strength to

methanoic acid. The dissociation constant of the acy form of dinitromethane is

$1.43 \cdot 10^{-4}$ at 0° and $2.8 \cdot 10^{-4}$ at 25°. In aqueous solutions of dinitromethane,

equilibrium exists between the true nitro compound and the acy form. In very dilute

solutions, this equilibrium is wholly shifted to the acy form:

$$H_2C(NO_2)_2 \rightleftarrows NO_2CH=NOOH \rightleftarrows NO_2CH=NOO^\ominus + H^\oplus.$$

When alkali is added, the equilibrium is shifted ▨X to formation of the acy form,

and when acid is added, in the direction of the true nitro compound. In a strong

sulfuric acid solution, dinitromethane exists only as the true nitro compound.(Bibl.30,

31).

In its chemical
▨▨▨▨▨▨▨▨▨▨▨ character, dinitromethane is a rather powerful monobasic acid.

An aqueous solution thereof yields an acid reaction to litmus paper and to methylorange.

In the presence of dinitromethane, free iodine is liberated from a mixture of potassium iodide and iodate ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXX~~ (Bibl.27). Dinitromethane decomposes salts of carbonic, sulfuric, and nitrous acids.(Bibl.26). It readily forms salts with inorganic and organic bases, for example, when mixed with ammonium, barium, and copper carbonates or hydroxides with dinitromethane in ether solution. An aqueous solution of its potassium salt yields a neutral reaction. The completely ~~XXXXXXXXX~~ pure potassium salt is stable and may be stored in the open air for a long time.

Salts of dinitromethane explode when heated to over 100°. When dinitromethane is reduced in an acid medium, ammonia is liberated, but if reduction is performed in water by a sodium amalgam, the result is so-called methylazouronic acid - a crystalline substance WX that explodes at 98°.

When dinitromethane is treated with bromine water, it converts to ~~XXXXXXXXXXXXXXX~~ dibromodinitromethane (Bibl.26). The effect of free halides upon the potassium salt of dinitromethane in the presence of caustic results in the formation of ~~XXXXXXXX~~ potassiumhalidedinitromethane ~~XXXXXXXXXXXXXXXX~~ (Bibl.32). However, if potassiumdinitromethane be treated with excess bromine in neutral solution, bromodinitromethane is formed (Bibl.33).

Dinitromethane readily reacts by condensation with formaldehyde and amines to form dinitroamines. It is capable of attaching to activated double bonds. Usually, the potassium salt of dinitromethane is employed for this type of reaction.

Dinitromethane is obtained by acidification of an aqueous solution of its potassium salt, accompanied by cooling. This latter is obtained in turn from the more accessible organic compounds, for example, dibromodinitromethane: $Br_2C(NO_2)_2$. Dinitromethane may also be obtained from symmetrical dipotassiumtetranitroethane:

$$KOON = C - C = NOOK \xrightarrow{H_2SO_4} 2CH_2(NO_2)_2.$$
$$\qquad\;\; | \quad | $$
$$\qquad NO_2\,NO_2$$

Section 3. <u>Trinitromethane</u>
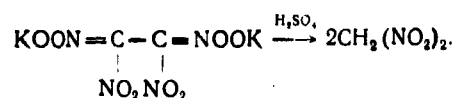
Trinitromethane $CH(NO_2)_3$ (nitroform) was first obtained in 1857 by L.N.Shishkov (Bibl.34). In view of the exceedingly high reactivity, &X it is capable of being widely used for the synthesis of polynitrocompounds. With this object, nitroform or a salt thereof is condensed with nitro compounds or aldehyde. Condensation with aldehydes results in the formation of nitro alcohols, the nitrates of which are powerful explosives.

Pure anhydrous nitroform is a colorless crystalline substance having a XXXXXXXXX characteristically sharp odor. The melting point is not exactly known, but it is apparently in the range of $23 - 25^\circ$ (Bibl.19, 35). The boiling point is $45 - 47^\circ$ at 22 mm Hg (Bibl.36). The specific gravity is $d_{40}^{25^\circ} = 1.61$ (Bibl.18).

Nitroform readily absorbs moisture, and acquires a yellow color as a consequence. It is readily soluble in water and in the common organic solvents. Solutions of nitroform in water, alcohol, acetic acid, and aqueous ether are yellow. Solutions in
anhydrous benzene, chloroform, carbondisulfide, ligroin, ether, and in strong sulfuric or hydrochloric acids, are colorless (Bibl.37). The yellow color relates to isomerization of the nitroform to the acy form:

$$H \cdot C(NO_2)_3 \rightleftarrows (NO_2)_2 C - N \overset{\displaystyle /\!\!/ O}{\underset{\displaystyle \backslash OH}{}}.$$
$$\quad I \qquad\qquad\qquad II$$
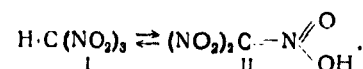
In aqueous, mildly acid, and basic media, the nitroform exists within the acy form. (II), and in a medium of very strong H_2SO_4, HNO_3, and other acids, as well as in the anhydrous condition, it exists in the form of nitro compound (I). The nitroform explodes when rapidly heated. An attempt to drive it off at atmospheric pressure results in decomposition at 100° (Bibl.34). The Nitroform may be distilled without decomposition. Under ordinary circumstances, it is relatively stable, and may be preserved without undergoing change, in the cold. Strong mineral acids decompose the nitroform (Bibl.34,37).

The nitroform is a very ~~strong~~ strong acid (Bibl.37). It readily forms salts with inorganic and organic bases. All these salts are substances light-yellow in color. They ~~lack~~ lack odor and have little stability in the dry condition. Inorganic salts decompose after a few hours, ~~converting~~ converting to nitrates in accordance with the equation:

$$2(NO_2)_2 C = NOOMe \rightarrow 2MeNO_3 + 2CO_2 + 2NO + N_2.$$
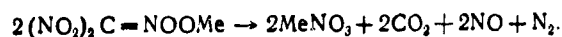
Solution of these salts in water is not accompanied even by the slightest signs of hydrolysis. The resultant yellow solutions have a neutral reaction.

The potassium, ammonia, and sodium salts of nitroform are obtained by reacting a weak solution of alkali with tetranitromethane in the presence of a reducing agent. This is a side process of the formation of the carbonate. The reaction goes as follows:

$$C(NO_2)_4 + 2KOH \rightarrow (NO_2)_2C = NO_2K + KNO_3 + H_2O;$$
$$C(NO_2)_4 + 6KOH \rightarrow 4KNO_2 + K_2CO_3 + 3H_2O.$$
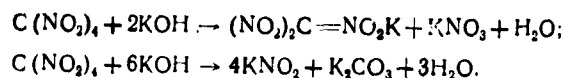
The potassium, sodium, and ammonia salts are derivatives of the acy form and are therefore yellow in aqueous solution.

The silver and mercury salts of the nitroform are tautomeric compounds capable of existing in two forms. Solutions thereof in ether, benzene, and chloroform are colorless. Salts freshly crystallized out of these solutions are also colorless crystals. Solutions in alcohols, acetone, and glacial acetic acid are weakly yellowish. Acqueous solutions are strongly yellow, carry electric current, and are quite acid.

Thus, the hydrogen of the nitroform is capable of being substituted for both in the acy form and in the pseudo form. Reaction with bases results in replacement of the hydrogen not only by metals or organic residues, but also by halides, for
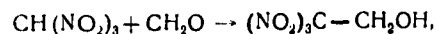
219   example, chlorine, with formation of chloropicrin:

$$C(NO_2)_3H + Cl_2 \rightarrow CCl(NO_2)_3 + HCl.$$
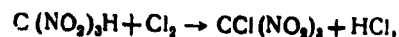
or by nitro group, with formation of tetranitromethane:

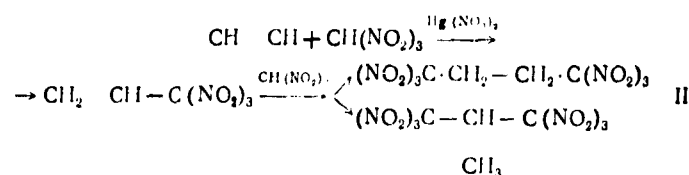$$C(NO_2)_3H + HNO_3 \rightarrow C(NO_2)_4 + H_2O.$$
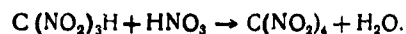
The nitroform is capable of undergoing condensation. Of particular interest is condensation thereof with formaldehyde, as a consequence of which trinitroethylalcohol is formed:

$$CH(NO_2)_3 + CH_2O \rightarrow (NO_2)_3C - CH_2OH,$$

220   which is a powerful explosive. Because of its hygroscopicity and low stability, it has not practical value.

The nitroform is capable of combining with unsaturated compounds at the double or triple bond. · For example, it combines with acetylene as follows:

$$
\begin{array}{c}
CH \quad CH + CH(NO_2)_3 \xrightarrow{\text{Hg}(NO_3)_2} \\
\rightarrow CH_2 \quad CH - C(NO_2)_3 \xrightarrow{CH(NO_2)_3} \left< \begin{array}{l} (NO_2)_3C \cdot CH_2 - CH_2 \cdot C(NO_2)_3 \\ (NO_2)_3C - CH - C(NO_2)_3 \\ \qquad\qquad CH_3 \end{array} \right. \qquad II
\end{array}
$$

Its salts, and particularly the silver salt, are capable of condensing with aromatic compounds.

The nitroform is an explosive. It can be detonated by shock or a capsule.

The simplest and most convenient method of producing the nitroform is decomposition of tetranitromethane by an aqueous solution of caustic potash. The reaction follows the following equation:

$$C(NO_2)_4 + KOC_2H_5 \rightarrow KC(NO_2)_3 + C_2H_5ONO_2.$$
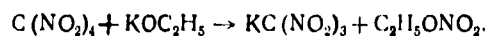
Free nitroform is liberated by adding XX excess strong sulfuric acid to an aqueous solution of a salt thereof:

$$KC(NO_2)_3 + H_2SO_4 \rightarrow HC(NO_2)_3 + KHSO_4.$$

220   The liberated oily product is extracted with ether. After the ether has been

driven off in vacuum, the nitroform remains as a volatile, bad-smelling oil, which,

after solidification in a freezing mixture and its separation over porous clay, forms

virtually colorless crystals that melt at 25°. The next Section describes the method

of obtaining the nitroform from acetylene.

Section 4. Tetranitromethane

Tetranitromethane $C(NO_2)_4$ was obtained in 1857 by L.N.Shishkov by the nitration

of trinitromethane (Bibl.34).

The absence of a dipole moment in tetranitromethane testifies to the symmetrical

structure of its molecule. This refutes the hypothesis of certain investigators to

the effect that the molecule contains one nitrite group O - NO and three nitro

groups - NO_2.

Tetranitromethane contains a considerable amount (about 50%) of active oxygen:

$$C \cdot (NO_2)_4 \rightarrow CO_2 + 2N_2 + 3O_2.$$

This property was employed in Germany to make jet fuels on the basis thereof

(Bibl.38).

Tetranitromethane is a very free-flowing, volatile, transparent, and colorless

liquid with a sharp odor. Its specific gravity is d_{40}^{15} = 1.65 (Bibl.39), its

freezing point 14.2° (Bibl.40), its viscosity at 20° is 0.0177 poise (Bibl.42). The

technical product freezes at 13.5 - 13.8°. The boiling point of tetranitromethane is

126 -127° (Bibl.41). Upon boiling, it partially decomposes into CO_2 and nitrogen

oxides.

Tetranitromethane is not hygroscopic, virtually insoluble in water, glycerol,

and other multiatomic alcohols. It is readily soluble in many organic solvents: toluene,

benzene, dichloroethane, etc., When these solutions are cooled below the freezing point

of tetranitromethane (below 13.5°), the solubility diminishes sharply, and the product

crystallizes out.

Several organic substances such as TNT, paraffin, and naphthalene, are miscible

with tetranitromethane in any ratios at temperatures above their melting points. Upon

cooling of these mixtures, the substances dissolved, crystallize out.

Tetranitromethane is insoluble in sulfuric acid. Nitric acid and tetranitromethane

are mutually soluble. At 15°, XX it dissolves 22 - 24 volumes of 98 - 98.6% HNO3. As

the strength of the HNO3 diminishes, its XX solubility diminishes. Tetranitromethane

readily dissolves nitrogen oxides, and a mixture of various volumes of these substances

has a freezing point of -36° (Bibl.43).

Tetranitromethane is volatile. Even at 0°, there is a perceptible odor reminding

one of the nitrogen oxides. It is readily distillable with steam. The fumes have an

irritating effect upon the mucuous membrane, cause tearing, running nose, and cough.

Continued inhalation of the fumes has a poisonous effect upon the organism.

Tetranitromethanes are readily absorbed by activated charcoal.

Pure tetranitromethane presents a neutral reaction. Upon standing it becomes

acid due to decomposition. Decomposition proceeds most actively in the presence of

water:

$$C(NO_2)_4 \overset{HOH}{\rightleftharpoons} CH(NO_2)_3 + HNO_3.$$
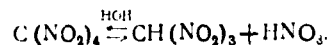
The quantity of acid products formed is readily determined by titration with

alkali. Both decomposition products: HNO3 and CH(NO2)3 IX are titrated (Bibl.44).

Decomposition of the tetranitromethane usually proceeds to equilibrium at an

acidity of about 0.1 - 0.2% in terms of HNO3. If the acid decomposition products are

424

221   removed by washing with water, decomposition of the next batch of tetranitromethane

will occur, and so forth until the entire product is decomposed.

Tetranitromethane is stable in acid media and may be stored for years in this

conditions. Therefore, the technical product is stabilized by acidification with

sulfuric acid, or with nitrogen XX oxides to an acidity of 0.1 - 0.2%. In this form,

it may be stored in iron apparatus.

Decomposition of tetranitromethane in an alkaline medium may be expressed by two

equations:

$$C(NO_2)_4 + 6KOH \rightarrow K_2CO_3 + 4KNO_2 + 3H_2O;$$
$$C(NO_2)_4 + KOH + C_2H_5OH \rightarrow C(NO_2)_3K + C_2H_5ONO_2 + H_2O.$$
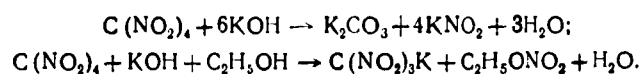
With aqueous solutions of alkalis, what occurs is primarily nitrite decomposition,

properties of
but with alcohol solutions it is nitroformed. The specific XXXXXXXX tetranitromethane

include its ability to produce a dark discoloration XX with organic substances containing

unsaturated bonds.

Tetranitromethane is a weak explosive, has little sensitivity to shock and to other

types of initial impulse. Its explosive properties, computed on the basis of the

theoretical decomposition equation, are the following: heat of explosive decomposition -

580 kcal/kg, temperature of explosion 2900°, volume of gaseous explosion products -

470 ltr/kg, velocity of detonation - 6300 m/sec.

Mixtures of tetranitromethane and organic substances are usually explosives. Some

100% in power. However,
of them exceed TNT by 50 to XXXXXXXXXXXXXXXXXXXXXXXX such mixtures are highly sensitive

and therefore very dangerous to handle.

222   Only substances XX soluble in tetranitromethane, but which do not react with it,

may be employed as fuels.

425

Pure tetranitromethane is a substance that presents virtually no danger. However,
in working with it, it is necessary XX rigidly to observe precautions, and completely
to eliminate the possibility of contamination of tetranitromethane by organic
substances of any kind.

Preduction of tetranitromethane. The literature describes more ten methods of
producing tetranitromethane, but only a few of these deserve attention from the view
point of recommendation for industrial purposes.

1. The acetic anhydride method. Acetic anhydride reacts with XXXXXXXXXXXX strong
nitric acid at 25 - 30°, in accordance with the following equation:

$$4(CH_3CO)_2 O + 4HNO_3 \rightarrow C(NO_2)_4 + 7CH_3COOH + CO_2.$$
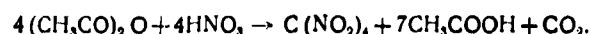
The initial substances are mixed in stoichiometric ratio, and are allowed to
stand from 5 - 7 days. The temperature of the reaction mixture has to be 25 - 28°.
After standing XXX for 5 - 7 days, the tetranitromethane liberated in the form of a
heavy oil on the bottom of the vessel. It is decanted steam-distilled. Tetranitromethane
XXXXX is purified by repeated steam distillation, and is dessicated with calcium
chloride. The product yield is 70 - 75% of the theoretical.

The raw
XXX materials consumed per ton of finished product are: 1.8 ton HNO_3 (monohydrate)
The
and 3 tons $(CH3CO)_2O$. Acetic anhydride may be recovered, in which case the absolute
consumption of acetic XXXX anhydride is about 0.6 ton.

duration
A shortcoming of the acetic anhydride method is the XXXXXX of the process.

2. Destructive nitration. When dinitrobenzene or other mono- and dinitro
severe
derivatives of the aromatic hydrocarbons are nitrated under XXXXXXXX conditions
(high-temperature, strong mixed acid), the reaction proceeds in two directions:

$$C_6H_4(NO_2)_2 \xrightarrow{HNO_3} C_6H_3(NO_2)_3 + H_2O;$$
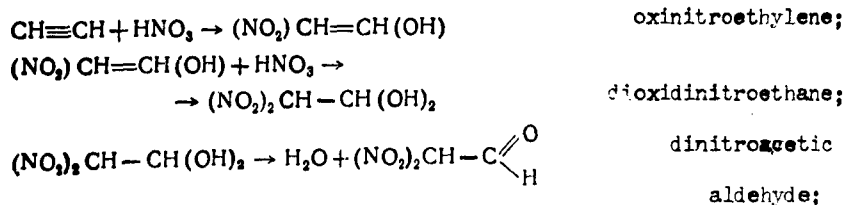$$C_6H_4(NO_2)_3 \xrightarrow{+12HNO_3} 3C(NO_2)_4 + 3CO_2 + 8H_2O + 2NO.$$
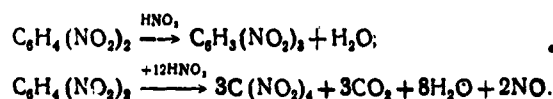
~~As a~~
~~The~~ consequence of the low yields of both products, the method is not economical.

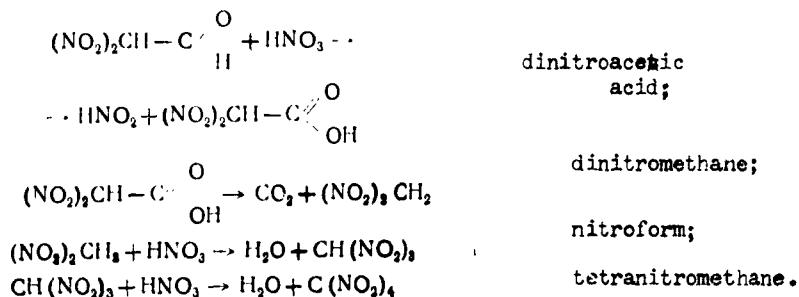Moreover, the process is very dangerous at high temperature.

3. **Nitration of acetylene** (Bibl.45, 46). The action of acetylene with strong

nitric acid proceeds through several stages and may be described by the following

summary equation:

$$5C_2H_2 + 38HNO_3 \rightarrow 3C(NO_2)_4 + 24H_2O + 7CO_2 + 26NO_2.$$
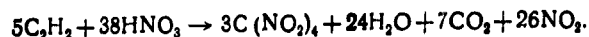
Thus, approximately 60% of the acetylene is converted into tetranitromethane, and

the remainder is oxidized. The process apparently may be expressed by the following

mechanism:

$$CH \equiv CH + HNO_3 \rightarrow (NO_2)CH = CH(OH) \qquad \text{oxinitroethylene;}$$

$$(NO_2)CH = CH(OH) + HNO_3 \rightarrow$$
$$\rightarrow (NO_2)_2CH - CH(OH)_2 \qquad \text{dioxidinitroethane;}$$

$$(NO_2)_2CH - CH(OH)_2 \rightarrow H_2O + (NO_2)_2CH - C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagdown}} \qquad \text{dinitroacetic aldehyde;}$$

$$(NO_2)_2CH - C\,\overset{O}{\underset{H}{\diagup}} + HNO_3 \cdot\cdot \qquad \text{dinitroacetic acid;}$$

$$\cdot\cdot HNO_2 + (NO_2)_2CH - C\overset{\displaystyle O}{\diagup}_{OH}$$

$$(NO_2)_2CH - C\overset{\displaystyle O}{\underset{\displaystyle OH}{}} \rightarrow CO_2 + (NO_2)_2CH_2 \qquad \text{dinitromethane;}$$

$$(NO_2)_2CH_2 + HNO_3 \rightarrow H_2O + CH(NO_2)_3 \qquad \text{nitroform;}$$

$$CH(NO_2)_3 + HNO_3 \rightarrow H_2O + C(NO_2)_4 \qquad \text{tetranitromethane.}$$

The last of these reactions occurs in the presence of sulfuric acid. Nitroform is

produced as an intermediate, and may be isolated by nitrogen dioxide extraction at 0°

(Bibl.38).

The possibility of converting acetylene to trinitro- and then to tetranitromethane

by nitric acid reaction was discovered in 1900. However, the product yield was

20 - 25%. In 1920, mercury nitrate came to be used as promoter, and the yield was
XXXXXX

223 increased to 40 - 45%. Subsequently, it was found that nitrogen ~~oxides have~~ a

positive effect upon the yield, and particularly upon the process rate. It was also

found that certain metals (Fe, Ni, Co, Al) are inhibitors of this process. Consideration

of these factors ~~made~~ it ~~made~~ possible to increase the yield of tetranitromethane

to 90%.

    4. Nitration of Ketene (Bibl.47). Tetranitromethane is obtained by slowly

admitting ketene (produced by pyrolysis of acetone) into cooled strong nitric

acid. At the conclusion of the reaction, the mixture is poured over ice, and the

tetranitromethane which settles out is separated. The yield is 90%. The reaction

follows this equation

$$4CH_2=CO + 4HNO_3 \rightleftharpoons C(NO_2)_4 + CO_2 + 3CH_3COOH.$$
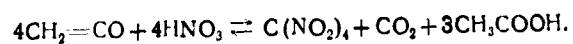
CHAPTER VII

GENERAL DESCRIPTION OF NITROAMINES

The polynitro derivatives of the amines are widely employed as high explosives.

This class includes RDX and TNT, which are brisant explosives widely employed in the

manufacture of detonators and caps, as well as in the filling of munitions.

The initial materials for the production of nitro amines are the amines of the

aromatic, heterocyclic, and aliphatic series, nitric, sulfuric, and, in a number of

instances, also acetic acid and acetic anhydride. The production of these explosives

is more dangerous than that of the nitro compounds in view of their high sensitivity

to temperature and mechanical influences, as well as their high tendency to detonate.

The polynitro amines are usually obtained by nitration of the corresponding amines,

in which the nitro group may replace either hydrogen at the carbon ($\equiv CH \xrightarrow[-H_2O]{+HNO_3} \equiv C - NO_2$),

or the hydrogen at the nitrogen ($= NH \xrightarrow[-H_2O]{+HNO_3} = N - NO_2$). In the first case, the result

is a C-nitro compound and in the latter a N-nitroamine.

The formation of nitro compounds under the effects of nitric acid or mixed acid

(so-called C-nitration) proceeds in accordance with the mechanism previously described.

The nitrating agent in N-nitration, when strong nitric acid or mixed acid is reacted

with an amino compound will also be the nitronium cation $NO_2^{\oplus}$ (Bibl.62), and the reaction

will also go in two stages: addition of $NO_2^{\oplus}$ and subsequent detachment of the

replaced hydrogen by the proton acceptor (Bibl.3). However, in performing this reaction,

224 it is necessary to take into consideration the presence ~~in~~ (of a) readily oxidized ~~xxxxx~~ amino

~~xxxxx~~ group in the compound. Therefore, in order to prevent or at least to reduce

oxidizing processes, the amino group is stabilized or as they say protected either° by

obtaining a salt (usually by means of sulfuric acid) or an acyl derivative (by ~~xx~~ means

of acetic acid). The product obtained is then nitrated.

 In N-nitration, reactivity ~~xxxxxxxxxxx~~ is higher than in C-nitration of the unsubstituted

benzene. Thus, for example, the unshared electrons of the nitrogen atom in ~~xxxxxxx~~

trinitrophenyl-N-methylamine are taken up by the the nitronium cation 1.5 times faster

than the unsaturated π-electrons in benzene, but at only ~~xxx~~ 1/17 the rate observed

in toluene (Bibl.3).

 According to Lang (Bibl.4), N-nitration caused by weak nitric acid occurs in the

presence of nitric oxides via the formation of the nitro derivative (by the effect of

225 the nitrosyl-cation $NO^{\oplus}$), which is also analogous to the mechanism of C-nitration.

 In choosing a solvent for nitration, it is necessary to bear in mind the possibility

that it may change the guiding effect of ~~xx~~ the amino group. In sulfates, the amino

or alkyl amino group direct the nitro group partly to the meta-position (Bibl.5), while

acylated alkyl amino groups are directed solely to the ortho- and in some degree to

the para-position.

 The direction of the nitro group entering the ring is determined in a number of

cases by the concentration of sulfuric acid in the nitrating mixture. Thus, if in

the nitration of acetanilide the nitrating mixtures include not 100% but 78.8% sulfuric

acid, the yield of para-nitroaniline will drop to 23.6%, with a corresponding rise in the

yield of the ortho-isomer. This is of practical significance, if we bear in mind that

the nitration process always is accompanied by the formation of water diluting the

NX

nitrating mixture.

In nitrating various aniline derivatives, it was observed that the formation of

the N-nitroamine facilitates the presence in the ring of a nitro group in meta-position
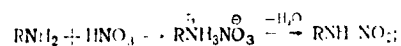
with respect to the amino group.

In some cases, N-nitration goes through the stage of salt formation. Thus, in

reacting dilute nitric acid with the amine, the consequence is a nitrate salt, because

of the fact that the amines are of weak basicity. Subsequent treatment of the salt thus

obtained with strong nitric acid or acetic anhydride (Bibl.⁴) results in the production

of N-nitroamine. It would appear that this stage involves a stage of dehydration

of the salt, accompanied by formation of N-nitroamine, for example, in accordance

with the reaction:

$$Ar - NH_2 \cdot HNO_3 \rightarrow Ar \cdot NH - NO_2 + H_2O.$$
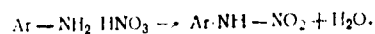
Some N-nitroamines, such as nitroguanidine, or nitro urea are produced

specifically via the nitrate salt as intermediate, dehydration of the salt being

performed by sulfuric acid.

The reaction follows these mechanisms:

for primary amines

$$RNH_2 + HNO_3 \rightarrow R\overset{+}{N}H_3 \overset{\ominus}{NO_3} \xrightarrow{-H_2O} RNH \cdot NO_2$$

for secondary amines

$$\underset{R}{\overset{R_1}{>}}NH + HNO_3 \rightarrow \underset{R}{\overset{R_1}{>}}\overset{+}{N}H_2 \overset{\ominus}{NO_3} \xrightarrow{-H_2O} \underset{R}{\overset{R_1}{>}}N \cdot NO_2.$$
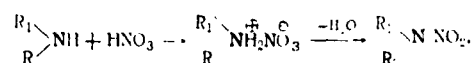
Secondary and tertiary aromatic amines, such as methylaniline, ethylaniline,

or diethylaniline are converted, by the vigorous effect of fuming nitric acid, to

monoalkyl-N-nitroamines, and, where the tertiary amines are concerned, cleavage of

one alkyl group occurs. Simultaneous with this, nitration of the aromatic ring

occurs (Bibl.7):

$$C_6H_5 - NH - CH_3 \xrightarrow[-H_2O]{+HNO_3} C_6H_2(NO_2)_3 N\begin{smallmatrix}CH_3\\NO_2\end{smallmatrix}.$$
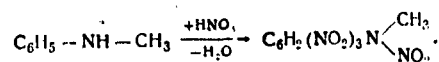
The entry of the nitro group into the ring of an aromatic amine, i.e., formation of the nitro compound, occurs as a consequence of two reactions: regrouping of phenylnitroamine (which is promoted by acid) and nitration by nitric acid. A.I.Titov (Bibl.9), and Hughes and Ingold (Bibl.10) hold that this regrouping is intramolecular in nature and proceeds through intermediate formation of cation by attachment of a proton to the amine nitrogen. This last explains the need to have an acid medium in order for this reaction to go. Subsequently, Hughes and others, employing tagged nitrogen, obtained direct proof of the intramolecular nature of the regrouping (Bibl.10).

Weakly basic amines nitrate readily, whereas strongly basic amines nitrate only in the presence of a promoter (chlorides are usually employed).

The amine nitration reaction is not infrequently accompanied by a breaking of the C-N bond, the consequence of which another organic molecule, most frequently alcohol, which is then etherified, is formed simultaneous with the N-nitroamine. Nitration with breaking of the C-N bond is called nitrolysis and may be depicted by the following mechanisms:

a) nitrolysis with alcohol formation

$$R_2NCH_2R' + HONO_2 \cdots R_2N - NO_2 + HO - CH_2R'$$
$$NO_2 - O - CH_2R';$$
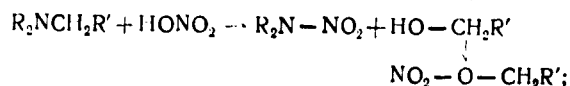
226   b) nitrolysis with formation of a free alkyl cation (forming a nitrate ester under the influence of the $NO_3^{\ominus}$ ion)

$$R_2NCH_2R' + NO_2^{\oplus} \rightarrow \begin{smallmatrix}R\\R\end{smallmatrix}\overset{\oplus}{N}\underset{NO_2}{\mid} - CH_2R' \rightarrow R_2N\cdot NO_2 + \overset{\oplus}{C}H_2R \underset{\downarrow + NO_3^{\ominus}}{} NO_2 - O - CH_2R.$$
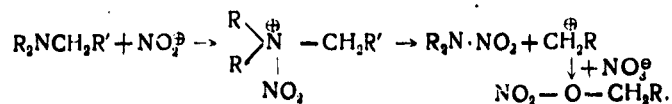
The reaction by which RDX is formed via nitration of urotropine, which detaches

the $-CH_2$, CH_2-, grouping, is a nitrolysis reaction. In addition to RDX, an alcohol

nitrate ester is formed, specifically, methyleneglycoldinitrate

$$CH_2 \diagdown {ONO_2 \atop ONO_2}$$
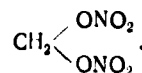
A considerable amount of nitrating agent is consumed in producing N-nitroamines,

and the reaction is usually run at low temperature, because of the low stability of

the side product. These process conditions result in a considerable consumption of

materials (raw material, cooling agent) when they are performed on a factory scale,

and lead to a high product cost.

On the industrial scale, the production of certain N-nitroamines, specifically

cyclotrimethylenetrinitroamine (hexogen) is conducted both by direct nitration of amines and

by an indirect method: condensation of formaldehyde with ammonium nitrate in the

presence of a promoter (BF_3). In some cases, this is economically more desirable than

direct nitration of the amine.

A. Lamberton (Pi. 1.11) holds that N-nitroamines may be regarded as amides of

ntric acid. If one hydrogen atom in the simplest inorganic N-nitroamine NH_2NO_2 be

replaced by alkyl or aryl groups, the result is the primary N-nitroamine $ArNH \cdot NO_2$.
If both
hydrogen atoms are replaced, the result is the secondary N-nitroamine

$Ar_2N \cdot NO_2$.

The nitroamides (primary and secondary) may be included among the N-nitroamines.

The difference between the two lies in the fact that in the latter, one group (Ar)

is acid (for example, acyl, sulfanyl, etc.).

The behavior of the C-nitroamines and their properties are analogous to the

properties of the nitro compounds, inasmuch as the nitro group therein is directly

attached to the carbon atom.

The behavior and properties of the N-nitroamines differ sharply from the

properties of the nitro compounds, as the nitro group therein is attached to the

nitrogen atom. This bond of the nitro group is weaker than a direct bond to carbon.

This is the reason, as a rule, for the fact that the N-nitroamines are less stable than

the nitro compounds. The N-nitroamines are usually more sensitive to mechanical

effects, and therefore many explosives of this class are employed to fill shells, only

in the phlegmatized form.

Characteristic reactions for the N-nitroamines are reduction by hydrogen and the

effect of sulfuric acid. When primary N-nitroamines are reduced, hydrazine derivatives

result, whereas the reduction of secondary N-nitroamines results in the formation of

alkylhydrazine. Vigorous reduction of alkylhydrazines results in reduction of

alkylamine and ammonia.

When strong sulfuric acid is reacted with N-nitroamines, the nitro group attached

to the nitrogen cleaves away. The primary N-nitroamines are particularly readily

subject to decomposition. Under the influence of dilute sulfuric acid, alcohol and

N_2O are form:

$$RNH \cdot NO_2 - \cdot ROH + N_2O.$$
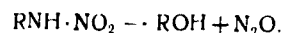
The secondary N-nitroamine are more stable to sulfuric acid and decomposition

frequently sets in only at high temperature.

Strong sulfuric acid induces cleavage of the N-nitroamines of the aliphatic or

heterocyclic series, accompanied by vigorous liberation of nitrous oxide. In some

cases, this reaction leads to the formation of N-nitrosoamines. This behavior of

N-nitroamines frequently renders it impossible to obtain them in sulfuric acid as medium.

There also exists a group of isomeric compounds with primary N-nitroamines, which also yield hydroxylamine derivatives on reduction. These compounds differ from the N-nitroamines in that the oxygen atoms are separated:

$$R - N - OH$$
$$\underset{NO}{|}$$
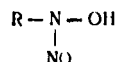
which is due to the manner in whi   they are obtained, to wit: nitrosification, and not nitration, as is the case of N-nitroamines.

The physical properties of the primary N-nitroamines are completely different than those of the nitroso derivatives of the hydroxylamines. For example, phenyl-N-nitroamines $C_6H_5NHNO_2$ differs substantially from phenyl-N-nitrosohydroxylamine.$C_6H_5\underset{NO}{N}OH$. The nitroso hydroxylamines have not yet been studied in terms of their explosive properties.

The structure of N-nitroamines, based on their chemical properties is confirmed by x-ray analysis of the simple N-nitroamines, which show that the atoms of the XXX $N-N\overset{O}{\underset{O}{\diagdown}}$ group are in a single plane (Pibl.12).

N-Nitroamines do not display basic properties, whereas the primary ones even have weak acid properties and are capable of yielding salts along with the bases. The acid properties of the primary N-nitroamines are only one **twentieth** XXXXXXXXXX as strong as those of formic acid. Contrariwise, nitroamides are capable of being strong acids, substantially more powerful than formic acid.(this is true for example of nitrourethane).

The primary XX N-nitroamines react readily with ammonia in a benzene medium, yielding ammonia salts. The majority of the N-nitroamines are subjected to denitration when heated with phenol, particularly in the presence of sulfuric acid.

435

227   Some of the aromatic N-nitroamines, for example, trinitrophenylmethyl-N-nitroamine

(tetryl), form addition products with the simplest amines. These ℵℵI addition products

are, for the most part, intensively colored. In many cases, these compounds convert

to picramide (2,4,6-trinitroaniline) or to its N-alkyl derivatives (Bibl.13).

THE CHEMISTRY AND TECHNOLOGY OF THE NITROAMINES

A. Tetryl and Other Nitro Derivatives of the Aromatic Amines

Tetryl was first obtained by Martens in 1877 by heating dimethylaniline with fuming nitric acid. Sometime later Romburgh (Bibl.1) determined the structure of tetryl, and obtained it by nitration of monomethyl- and dimethylaniline. From the fact that nitration of dimethylaniline reveals the formation of CO_2 and abundant liberation of nitrogen oxides, which is hardly to be noticed in the nitration of monomethylaniline, he drew the conclusion that tetryl contains only one methyl group. he found it possible to reinforce this point of view by obtaining tetryl from N-methyl- and N-dimethylpicramide, as well as from picryl chloride and potassium methylnitroamine. Romburgh ascribed the following formula to tetryl: $C_6H_2(NO_2)_3N\begin{subarray}{l} CH_3 \\ NO_2 \end{subarray}$, and it is still accepted today.

22. The explosive properties of tetryl were studied in 1885 - 1886 in the Prussian Department of War by Lenz, who found that tetryl was unsuited to filling shells because of its high sensitivity to friction.

Tetryl has a good sensitivity to detonation, and therefore, starting in 1906, it came into use in detonators and detonating caps. Today, tetryl is of secondary importance, and its production and consumption are being reduced.

Section 1. The Chemistry of Production, the Properties, and the Applications of Tetryl

Tetryl (trinitrophenylmethyl-N-nitroamine) may be obtained from dimethylaniline, monomethylaniline, and benzene (via dinitrochlorobenzene). Its structural formula is

$$CH_3 \quad NO_2$$
$$N$$
$$O_2N \quad | \quad | \quad NO_2$$

$$NO_2$$
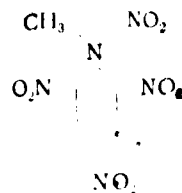
a) Production of Tetryl from Dimethylaniline

On the industrial scale, dimethylaniline is produced by passing aniline bases with methylether (a methanol-production waste) over active aluminum oxide at 230 - 295°. Contact alkylation of aniline by dimethylether makes it possible to produce XX dimethylaniline which is virtually free of aniline and monomethylaniline as impurities (Bibl.2,3,4,5).

Dimethylaniline is colorless liquid boiling at 193.5°, having a freezing point of +1.96°, and a specific gravity of 0.955. The technical product is from yellow to brown in color.

The highly reactive amino- or alkylated amino group greatly increases the ability of the benzene ring to undergo oxidation and resinification. The para-position relative to dimethylamine group is the most reactive in dimethylaniline. Thus, when nitrous acid is reacted with dimethylaniline, green para-nitrosodimethylaniline is formed:

$$N(CH_3)_2 \qquad N(CH_3)_2$$
$$\bigcirc \quad + HONO \rightarrow \quad \bigcirc \quad + H_2O.$$
$$NO$$
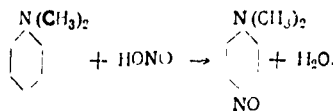
Dimethylaniline, as a ternary aliphatic-aromatic amine, reacts in one of two ways with concentrated sulfuric acid: it either forms a salt - dimethylanilinesulfate, or dimethylanilinesulfonic acid. The temperature determines the direction in which the reaction goes. At low temperature, (the salt is formed, and at) high temperature (of the order

of 180 - 190°), para-sulfonic acid is formed:
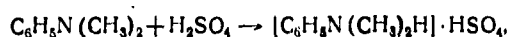
$$N(CH_3)_2 + H_2SO_4 \rightleftharpoons \quad + H_2O.$$

(with SO₃H group shown on ring)
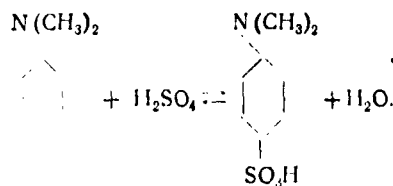
229   Dimethylaniline-para-sulfonic acid is a colorless crystalline mass which fuses XXXXXXXXXXXXXXX (acquiring a dark shade) at 257°.

At low temperature (40°), dimethylaniline forms a XXXXX salt with sulfuric acid:

$$C_6H_5N(CH_3)_2 + H_2SO_4 \rightarrow [C_6H_5N(CH_3)_2H] \cdot HSO_4,$$

which, at high temperature (over 100°) is capable of undergoing conversion to

dimethylaniline sulfonic acid in accordance with

$$[C_6H_5N(CH_3)_2H] \cdot HSO_4 \rightarrow C_6H_4(SO_3H) \cdot N(CH_3)_2 + H_2O.$$

The sulfate salt dimethylaniline is a colorless crystalline material having a

melting point of 91.5°. It is very hygroscopic, dissolves readily in sulfuric acid,

water, and alcohol. Bases cause it to decompose, with liberation of free dimethylaniline.

As the salt of a weak base and a strong acid, it hydrolizes readily, to yield an acid

reaction.

When dimethylaniline is nitrated with weak XXXXXXXXX nitric acid (50%) or mixed

sulfuric and nitric acids, at low temperature (0°), mononitrodimethylaniline is obtained

$$C_6H_5N(CH_3)_2 + HNO_3 \rightarrow C_6H_4(NO_2)N(CH_3)_2 + H_2O$$

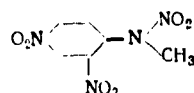as is dinitrodimethylaniline

$$C_6H_3(NO_2)_2N(CH_3)_2.$$
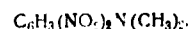
According to Orton (Bibl.6), the presence of nitrous acid is required to nitrate

dialkylanilines. In his opinion, an intermediate may come into being here - the

nitroso compound $ON \cdot C_6H_4 \cdot N(CH_3)_2$, which is subsequently oxidized to the nitro

XXXXXXXXX
compound

XXXXX compound. A study by Lang (Bibl.7) gives some support to this view. Lang

reacted nitric acid with dimethylaniline to produce a mixture of di- and

trinitrophenylmethyl-N-nitrosoamines:
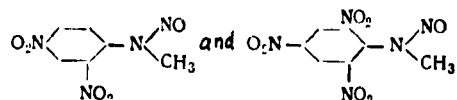
Stronger nitric acid results in the formation of dinitrophenylmethyl-N-nitroamine

Later, (Bibl.8,9) it was determined that the reaction of conversion of XXXXXXX

dinitrodimethylaniline to tetryl is promoted by nitrogen oxides (nitrous acid) which,

at the same time, constitute a powerful demethylating agent.

Hodgson (Bibl.10) and Urbanskiy (Bibl.11) having studied the effect of nitric
                                                                                        of
acid XXX various concentrations upon dimethylaniline, found that at 0°, reaction of

99.6% nitric acid results in the formation of N-nitro-2,4,6-trinitromethylaniline;

                                                                    54% and 40% nitric acid
70% nitric acid yields 2,4,6-trinitromethylaniline; XXXXXXXXXXXXXXXXXXXXXXXX yields

2,4-dinitrodimethylaniline, and reaction of 20% nitric acid yields a mixture containing

about 40% 3,3',5,5'-tetranitro-N,N,N',N'-tetramethylbenzidine and about 60%

2,4-dinitrodimethylaniline. The reaction does not occur if the nitric acid is weaker.

With increase in temperature, cleavage of the methyl group is observed, as is the case

when 50% and 40% nitric acids are used. With 20% nitric acid, it is only nitration

that occurs.

Sodium nitrite accelerates the reaction, and urea has the opposite effect.

Comparative tests show (Bibl.8), that nitrous acid is a more effective

demethylating agent than is nitric acid.

The sequence of nitration of dimethylaniline by nitric acid may be represented
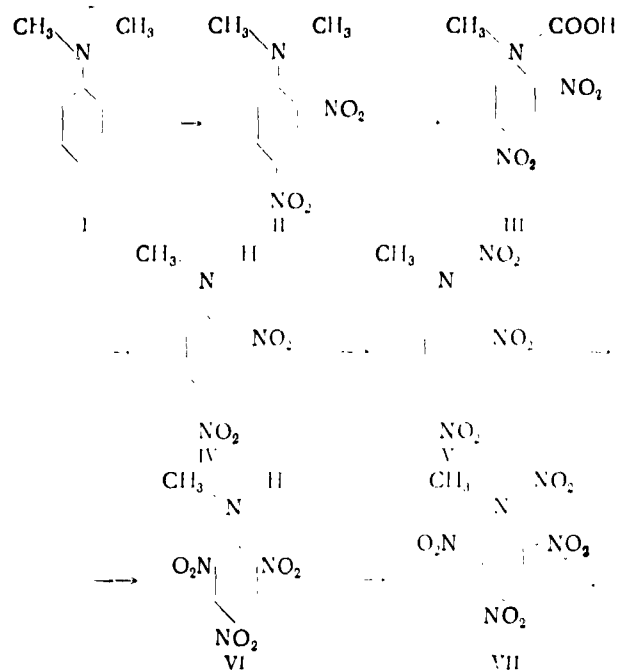
by the following mechanism (Bibl.8,10):

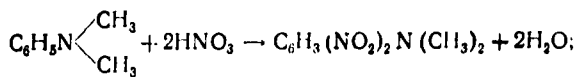Table 76 presents the properties of the nitro derivatives of dimethylaniline.

Table 76

Compound	Melting Point, °C	Appearance
Para-nitrodimethylaniline	161 – 162	Yellow crystals with steely cast
Ortho-nitrodimethylaniline	20	Free-flowing orange oil
Meta-nitrodimethylaniline	60 – 61	Red crystals
2,4-Dinitrodimethylaniline	87	Bright yellow crystals
2,6-Dinitrodimethylaniline	78	–
3,4-Dinitrodimethylaniline	174 – 175	–
3,5-Dinitrodimethylaniline	112	–

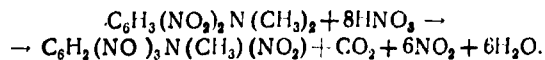When dimethylaniline is nitrated in two stages (Bibl.10), first by weak, and

then by strong nitric acid or mixed acid, the tetryl is obtained by the following
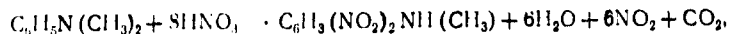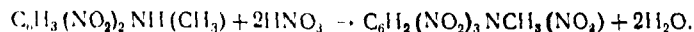
230   probable ▨▨▨▨ mechanism:

first stage

$$C_6H_5N\diagdown\begin{matrix}CH_3\\CH_3\end{matrix} + 2HNO_3 \rightarrow C_6H_3(NO_2)_2N(CH_3)_2 + 2H_2O;$$

second stage

$$C_6H_3(NO_2)_2N(CH_3)_2 + 8HNO_3 \rightarrow$$
$$\rightarrow C_6H_2(NO)_3N(CH_3)(NO_2) + CO_2 + 6NO_2 + 6H_2O.$$

231   On the industrial scale, this method is not employed, due to the large consumption

of acids (ratio of mixed acid to dimethylaniline 50:1). A smaller consumption of

concentrated acid occurs when the process is run in such fashion as to cause oxidation

of the methyl group in accordance with the equation

$$C_6H_5N(CH_3)_2 + 8HNO_3 \cdot C_6H_3(NO_2)_2NH(CH_3) + 6H_2O + 6NO_2 + CO_2,$$

and in the second phase, there is further nitration:

$$C_6H_3(NO_2)_2NH(CH_3) + 2HNO_3 \rightarrow C_6H_2(NO_2)_3NCH_3(NO_2) + 2H_2O.$$

However, this variant of the process is also quite complex in the ▨▨▨K technological

sense. ▨▨▨

In industry, tetryl is obtained from dimethylaniline in two stages. In the first

stage, dimethylaniline is converted to the sulfate salt by treatment with commercial

sulfuric acid. In the second stage, the dimethylaniline sulfate obtained is nitrated

with concentrated nitric acid or melange. Running the process in this way is most

practicable, inasmuch as the activating effect of the amino group, causing the oxidizing

processes, is diminished by conversion to the more stable sulfate salt. This may be

seen from the following example: dimethylaniline added to the melange (at 20 - 40°)

immediately flashes with formation of an oily black substance, while ▨▨▨▨▨▨▨▨▨▨▨▨▨▨▨▨▨▨

dimethylanilinesulfate nitrates to tetryl under these conditions.

231   Theoretically, production of dimethylanilinesulfate requires 0.81 part H_2SO_4 by

weight per part dimethylaniline. However, in practice, 8 parts sulfuric acid is

employed by weight, i: the form of 93 - 94% commercial sulfuric acid. The large excess

of sulfuric acid makes for complete conversion of the dimethylaniline to salt, and its

solution in excess acid. The excess acid goes to strengthen the mixed acid. Reduction

in the amount or concentration of the sulfuric acid may lead, on the one hand, to

incomplete neutralization, which in turn results in XXXXX flash when the salt is

run into melange, while on the other hand it results in producing weak mixed acid,

inducing premature oxidation, foaming of the nitro mass, and reduction of the quality
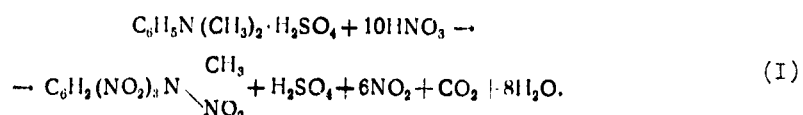
of the tetryl. XXX

The process of neutralization runs at 35 - 40°. Increase in temperature may

induce partial resinification of the dimethylaniline, as well as the formation of

sulfonic acid, nitration of which yields unstable side products and reduces the tetryl

yield.

Production of the sulfate salt dimethylaniline is a very critical operation, and

the skill with which it is performed governs the yield of tetryl, as well as the safety

of the process, to a considerable degree.

The conversion of dimethylaniline to the salt IX may be checked by the appearance

of the reaction liquid: transluscence and the lack of oily spots on the surface when

diluted with water is a reliable proof of the absence of free dimethylaniline.

Dimethylanilinesulfate may be nitrated either by concentrated nitric acid or by

melange. Nitration with melange goes more quietly, as the nitrogen oxides are in the

form of nitrosyl sulfuric acid. However, upon nitration with nitric acid, the nitrogen

oxides contained therein give rise to resinification of dimethylanilinesulfate.

443

231 When tetryl is formed from dimethylanilinesulfate, two reactions occur: nitration

and oxidation. One of the methyl groups is subjected to oxidation, and a nitro group

has to take its place. Oxidation of the methyl group g̶o̶e̶s̶ thanks to the nitric acid,

which is reduced to NO_2 and NO. Depending upon the degree of reduction X̶X̶ of the

232 nitric acid, the consumption will vary and the reaction will be expressed by one of

two equations:

$$C_6H_5N(CH_3)_2 \cdot H_2SO_4 + 10HNO_3 \rightarrow$$
$$\rightarrow C_6H_2(NO_2)_3 N\begin{smallmatrix}CH_3\\\\NO_2\end{smallmatrix} + H_2SO_4 + 6NO_2 + CO_2 + 8H_2O. \qquad (I)$$
$$C_6H_5N(CH_3)_2 \cdot H_2SO_4 + 6HNO_3 \rightarrow$$
$$\rightarrow C_6H_2(NO_2)_3 N\begin{smallmatrix}CH_3\\\\NO_2\end{smallmatrix} + H_2SO_4 + 2NO + CO_2 + 6H_2O. \qquad (II)$$
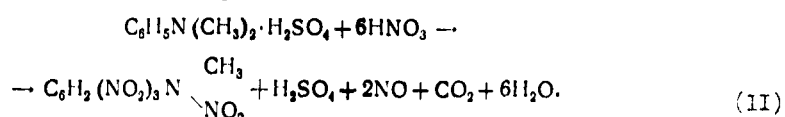
When the reaction follows the first equation, 5.2 parts nitric acid monohydrate

are X̶X̶ required per part by weight of dimethylaniline. In practice, it is this ratio

that is employed. However, the residue of nitric acid remaining in the X̶X̶X̶X̶ spent

acid (as much as 8%) indicates that the reaction goes, in part, in accordance with

the second equation.

In nitration of dimethylanilinesulfate, the nitro groups obviously enter the ring

at the outset. Upon entry of electrically negative NO_2 groups into the benzene ring,

the major properties of dimethylaniline disappear, the existence of the sulfate salt

becomes impossible, and the attached sulfuric acid detaches. At this time, the mixed

acid is diluted somewhat with reaction water, and its oxidizing effect increases.

Subsequently, oxidation of one methyl group to carboxyl, X̶X̶X̶ with subsequent

detachment of CO_2, sets in. X̶X̶

Despite the fact that the activating effect of the displaced amino group is

232   substantially diminished by the attachment of sulfuric acid in dimethylanilinesulfate,

this salt nevertheless oxidizes and resinifies rather easily, and therefore nitration

has to be conducted with great care. Nitration is performed by running in a sulfate

solution of dimethylaniline salt to melange in the nitrator. If the reverse procedure

were used in run-in, powerful oxidizing processes would occur, and ignition of the

product might occur.

Nitration is performed in a specific temperature interval (50 - 60°) and deviation

from this results in pronounced change in the process. Reduction in the temperature

of onset of nit   on inhibits oxidation of the methyl group and therefore, even an

increase in the time does not make it possible to obtain XX high yield and good-

quality tetryl. Moreover, at low temperature, in view of the negligible reaction

velocity, unreacted product accumulates in the apparatus, and this presents a great

danger. Nitration at higher temperature results in deeper XX oxidation than is required

for the production of tetryl, and therefore results in a reduction in yield and

impairment of the quality of the latter. Tetryl produced at high temperature is darker

in color, due to the partial resinification.

The temperature of 150°, at which flash of the reaction mass occurs, is critical.

From the point of view of safety, nitration is best performed at 60°. XXX Under these

conditions, most of the component mixture is able to react during run-in, and if

cessation of stirring or cooling occurs, the heating of the mass due to continued

reaction will be small.

The unpurified tetryl obtained _from_ dimethylaniline contains a small quantity of

impurities, which reduce its freezing point by 1.5 - 2°.

The major impurity is tetranitrophenylmethyl-N-nitroamine (meta-nitrotetryl), in

which the nitro group in the meta-position is readily replaced by hydroxyl when boiled

with water, and forms trinitromethyl-N-nitroaminophenol
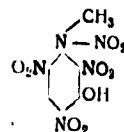
Thanks to the presence of three nitro groups in the ring, the hydrogen atom of

the hydroxyl has a pronounced acid nature, in connection with which trinitromethyl-N-

nitroaminophenol has the properties of a ~~XXXXXXXX~~ strong organic acid and communicates

residual acidity to tetryl.

Trinitromethyl-N-nitroaminophenol reacts freely with alkalis, carbonates, and

metal oxides, to form phenolates.

An increase in the yield of ~~XX~~ metanitrotetryl is faciliated by the use of low-grade

dimethylaniline, containing up to 0.3% monomethylaniline, as well as by the use of

mixed acid of increased strength or by ~~XX~~ increasing the quantity of sulfuric acid

therein, ~~XXXX~~ inasmuch as, under these conditions, there is an increase in the

meta-orienting effect of the $N(CH_3)_2 \cdot H_2SO_4$ group.

According to Romburgh (Bibl.12), the formation of meta-nitrotetryl proceeds

through the formation of mononitromethylaniline:
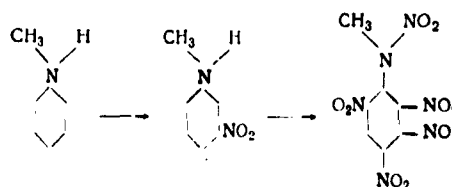
An increase in the temperature of nitration also makes for an increase in the

yield of meta-nitrotetryl.

Meta-nitrotetryl diminishes the stability of tetryl. With a 1% meta-nitrotetryl

content, the time required for an Abel spec. on iminishes to 15 min (instead of

233   25 min), and when the content is 10%, it is reduced to three minutes. According to

Obermueller, meta-nitrotetryl yields an increase in pressure of 588 mm per hr, while

purified tetryl causes a rise of only 20 - 30 mm. Thus, meta-nitrotetryl decomposes

25 times more rapidly than does tetryl.

Meta-nitrotetryl also is responsible for the acidity of tetryl, inasmuch as, when

reacted with water, it hydrolizes to XXXXX nitrous acid and trinitromethyl-N-

nitroaminophenol. Meta-nitrotetryl also affects the color of tetryl to a considerable

degree, giving it a bright greenish tint under certain circumstances.

The yield of meta-nitrotetryl may be reduced by employing quality dimethylaniline,

not containing monomethylaniline, and by the XXXX use of a less concentrated mixed acid.

However, this results in turn, in increasing the contents of incomplete nitration

products in the tetryl, which results in a reduction in the quality and the yield of

the basic product.
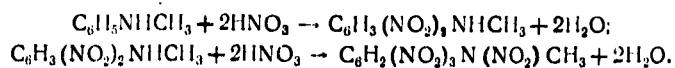
h) Production of Tetryl from Monomethylaniline

Monomethylaniline is obtained by passing an XXX alcohol solution of aniline,

containing PCl_3 through a system of autoclaves (Bibl.13), or by reacting an aqueous

methylamine solution upon chlorobenzene in the presence of combined copper (Bibl.14).

Monomethylaniline is a transparent liquid ranging from yellow to brown in color,

boiling at 195.5°. Its freezing point is -57°, and its specific gravity is $d_{4°}^{20°} = 0.989$.

The chemical properties of monomethylaniline are very similar to those of dimethylaniline.

However, monomethylaniline is XXXXXXXX somewhat more reactive than dimethylaniline.

This is expressed, in part, by the XXX fact that it oxidizes more readily and resinifies

upon reaction with nitric acid.

Martens, nitrating monomethylaniline with weak nitric acid (10 parts 50% HNO_3 by

XXX

447

233   KX weight per part monomethylaniline) obtained trinitromonomethylaniline.

234   Desvergnes (Bibl.15) developed a two-stage method of nitration of monomethylaniline

to tetryl. The following reactions occur therein:

$$C_6H_5NHCH_3 + 2HNO_3 \rightarrow C_6H_3(NO_2)_2 NHCH_3 + 2H_2O;$$
$$C_6H_3(NO_2)_2 NHCH_3 + 2HNO_3 \rightarrow C_6H_2(NO_2)_3 N(NO_2)CH_3 + 2H_2O.$$

As is evident from the equations adduced, it is not necessary, in nitrating

monomethylaniline, to expend nitric acid upon the oxidation of the methyl group, and

therefore, the consumption thereof has to be considerably less than in the nitration

of dimethylaniline. This makes for what is indubitably XXXX an expedient process.

However, this process has not come into practical use, apparently because of the

complexity of work with dilute nitric acid. However, the nitration of monomethylaniline

through the sulfate salt stage, as occurs when tetryl is made from dimethylaniline may

result in the production of a considerable amount of meta-nitrotetryl.

Table 77 presents some of the properties of the nitro derivatives of XXX

monomethylaniline.

Table 77

Compound	Melting point, $^{\circ}C$	Appearance
Para-nitromonomethylaniline	150 - 151	Yellow-brown crystals with violet shading
Ortho-nitromonomethylaniline	34 - 35	Red crystals with violet shading
Meta-nitromonomethylaniline	65 - 66	Reddish-yellow crystals
2,4-Dinitromonomethylaniline	176.7	Canary yellow crystals
2,6-Dinitromonomethylaniline	106	–
2,5-Dinitromonomethylaniline	161	–

When monomethylaniline is nitrated to tetryl, the following amounts of heat are

liberated (Bibl.16):

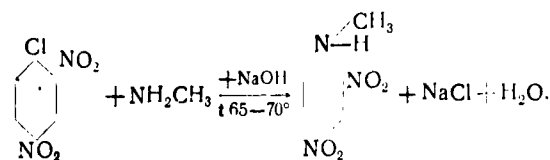methylaniline to para-nitromethylaniline – 36.4 kcal/mole; para-nitromethylaniline

448

to 2,4-dinitromethylaniline - 25.2 kcal/mole; 2,4-dinitromethylaniline to 2,4,6-

trinitromethylaniline ~~XXXXXX~~ - 11.9 kcal/mole; 2,4,6-trinitromethylaniline to

tetryl - 1.0 kcal/mole.

                   tetryl
c) Production of ~~XXXXX~~ from chlorobenzene and methylamine. Synthesis of tetryl

from chlorobenzene goes through a number of stages:

    1) production of dinitrochlorobenzene

$$C_6H_5Cl + 2HNO_3 \rightarrow C_6H_3(NO_2)_2Cl + 2H_2O;$$
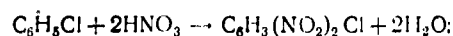
    2) production of dinitrophenylmethylaniline (melting point 176.7°) (Bibl.17)

                                                     xxx able
The reaction of replacement of chlorine by the alkylamino group ~~rather~~ to be

                              catalyst
run in organic solvents with copper ~~used as promoter~~ (Bibl.18).

Nitration of dinitromonomethylaniline by mixed acid containing 16 - 17% water

                                      having
at 30 - 40° results in a 95% yield of tetryl ~~having~~ a melting point of 128.1- 128.4°

                of
(Bibl.19). This method/producing tetryl is less dangerous than production from

dimethylaniline. A considerable advantage therein also lies in the fact that

dinitrochlorobenzene is simultaneously an intermediate product for production of

synthetic dyes. The second starting product - methylamine-is, under standard

conditions, a gas, and is usually employed either as a salt (sulfate) or as an

aqueous solution (solubility in 100 gm of water at 25° is 959 cm³, and in ether

solubility is virtually unlimited   ).

    The ~~XXXXXX~~ specific gravity of methylamine Π is $d_{4°}^{-70°} = 0.7691$, its melting

point is 92.5°, and is boiling point 6.5°.

Methylamine is produced by reacting formaldehyde with ammonium chloride

(Bibl.20) or from acetic acid and ammonia.

Properties of tetryl. Tetryl is a white crystalline substance. The technical

product is bright yellow. The specific gravity of tetryl is 1.73, and its

gravimetric density is $0.9 - 1$ gm/cm^3. Tetryl is readily ~~susceptible to passing~~

to a density of $1.60 - 1.63$ gm/cm^3 (at $P = 2000$ kg/cm^3 ~~XXXXXXXX may be pressed~~ to

1.71).

The melting point of tetryl is $129.45°$ (fusion is accompanied by decomposition),

the freezing point of chemically pure tetryl is $128.5°$, and that of technical

tetryl $127.7°$. The specific heat capacity of tetryl at $20°$ is 0.218 kcal/gm$°$C

(Bibl.21). Its melting point is 20.6 kcal/gm.

~~XXXXXXXX~~ Tetryl is nonhygroscopic, and very slightly soluble in water

(0.019% at $50°$, and 0.184% at $100°$). The solubility of tetryl in various solvents

is presented in Table 78.

Tetryl is a neutral substance and does not react with metals, but does

react with alkalis and sodium and potassium carbonates. When tetryl is heated

with dilute solutions of alkalis, picrates result (Bibl.22):

$$C_6H_2(NO_2)_3 N\!\!<^{CH_3}_{NO_2} + 2NaOH \rightarrow NaNO_3 + CH_3NH_2 + C_6H_2(NO_2)_3 ONa.$$
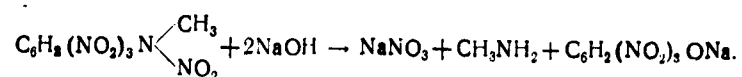
When tetryl is heated with water over a long period, it decomposed slowly

to form picric acid.

The addition of up to 10% sodium picrate virtually does not change the shock

sensitivity XX of tetryl, but merely reduces its melting point by $0.6°$. Therefore,

soda has been used in France to accelerate the washing of acids out of tetryl

(Bibl.23).

With alcohol solutions of alcoholates, a toluene solution of tetryl forms

metallic derivatives, usually the metallic derivatives of trotyl.

The metallic derivatives of tetryl are carmine red substances having a

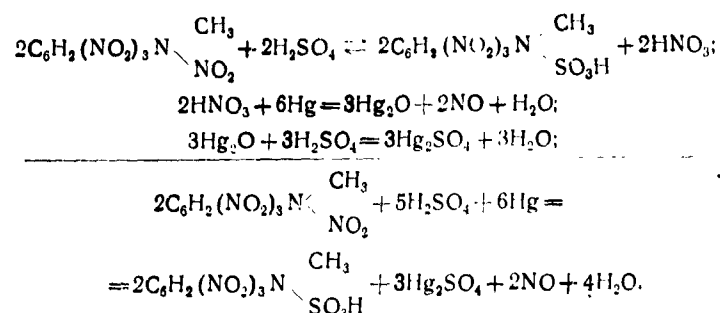flash point between 93 - 115°., and similar to mercury ~~fulminate~~ fulminate in shock

sensitivity

Table 78

a)	b)							
	c)	d)	e)	f)	g)	h)	i	j)
0	0,005	3,45	—	1,5	0,32	0,007	0,188	0,009
17	0,007	—	—	—	0,49	0,020	—	0,017
20	0,008	9,99	45,82	3,8	0,56	0,025	0,418	0,021
30	0,008	—	—	—	0,76	0,039	0,493	0,029
40	0,011	—	—	7,7	1,12	0,058	—	0,056
45	0,014	—	—	—	1,38	0,073	—	0,094
50	0,019	—	111,85	—	1,72	0,095	—	—
60	0,035	—	—	18,8	2,64	0,154	—	—
70	0,053	21,86	—	—	4,23	0,241	—	—
75	0,066	—	—	—	5,33	0,297	—	—
80	0,081	42,43	—	64,5	—	—	—	—
100	0,184	—	—	—	—	—	—	—

a) Temperature, °C; b) Grams of tetryl dissolving in 100 cm^3 of;

c) Water; d) Benzene; e) Acetone; ~~XXBIXXIXXXXXXX~~ f) Dichloroethane;

g) Alcohol; h) Carbon tetrachloride; i) ~~XXXXXX~~ Ether; j) Carbon disulfide

235   When gaseous ammonia is admitted in the cold into an alcohol acetone solution

of tetryl, the solution becomes dark red. Heating results in the gradual

disappearance of the red coloring and the ~~IX~~ liberation of picramide (Bibl. 24):

CH₃   NO₂   NH₂

    N
O₂N   NO₂ NH₃ O₂N   NO₂

    NO₂   NO₂
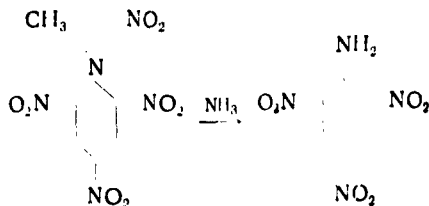
In the presence of metallic mercury, sulfuric acid liberates one atom
of nitrogen from tetryl in the form of nitrogen oxide. According to the data
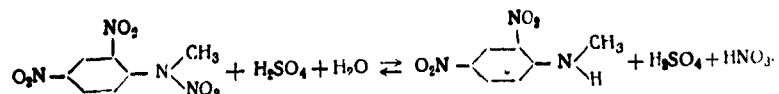of A.A.Solonina, the following reactions occur accompanying this:

$$2C_6H_2(NO_2)_3N\diagdown\begin{matrix}CH_3\\NO_2\end{matrix}+2H_2SO_4 \rightleftarrows 2C_6H_2(NO_2)_3N\diagdown\begin{matrix}CH_3\\SO_3H\end{matrix}+2HNO_3;$$

$$2HNO_3+6Hg=3Hg_2O+2NO+H_2O;$$

$$3Hg_2O+3H_2SO_4=3Hg_2SO_4+3H_2O;$$

$$\overline{2C_6H_2(NO_2)_3N\diagdown\begin{matrix}CH_3\\NO_2\end{matrix}+5H_2SO_4+6Hg=}$$

$$=2C_6H_2(NO_2)_3N\diagdown\begin{matrix}CH_3\\SO_3H\end{matrix}+3Hg_2SO_4+2NO+4H_2O.$$

The reaction of tetryl with sulfuric acid, leading to the formation of

trinitrophenylmethyl sulfamine, also occurs in the absence of mercury, but this

is apparently a reversible reaction, and the equilibrium is shifted sharply from

right to left. However, in the presence of mercury, when HNO_3, which reacts with

it, is eliminated from the sphere of ~~FULL~~ reaction, the equilibrium shifts from

left to right.

We know, that when concentrated sulfuric acid acts upon dinitrophenylmethylnitro-

amine (in the absence of nitric acid), regrouping occurs, as a consequence of which

~~XXIXIXXXXXXXXXI~~ trinitrophenylmethylamine is formed by the following mechanism
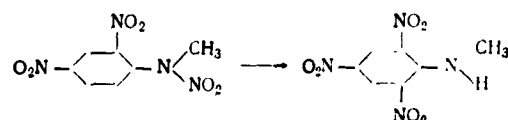
The weak (not over ~~XXXIXXXXX~~ 70%) sulfuric acid does not cause this

~~XXXXXXXXX~~ rearrangement, but merely the expulsion of the nitro group from the

side chain, with formation of dinitrophenyl methylamine:

$$O_2N-\langle\;\rangle-\overset{NO_2}{N}\!<^{CH_3}_{NO_2} + H_2SO_4 + H_2O \rightleftarrows O_2N-\langle\;\rangle-\overset{NO_2}{N}\!<^{CH_3}_{H} + H_2SO_4 + HNO_3.$$

In tetryl, all the ortho- and para-positions in the ring, with respect to the amino group, are occupied, and therefore, not XXXXXX only weak, but concentrated sulfuric acid will result not in rearrangement, but expulsion of the nitro group at the nitrogen.

With X9 68% trotyl, tetryl forms a eutectic mixture melting at 6^{r} - 68.5^{o} (Bibl.25).

Tetryl is more poisonous than trotyl and particular care must be exercised in working with it (Bibl.26).

237   The stability of tetryl is somewhat lower than that of trotyl and other nitro compounds, but it is nevertheless sufficient for long-term storage under normal conditions.

Okhta
According to the data of the laboratory of the XXXXX XXXXX Works (Bibl.23), tetryl withstood the Abel test (at 100°) for 20 min after being heated for 2 yrs at 60°. When tetryl was held at 75° for 320 days, the weight loss was 0.3%, but at 110° it attained 11.5% within only 16 days.

The shock sensitivity of tetryl is higher than that of trotyl and nitric acid. Tetryl explodes when a XXX 2-kg weight is dropped from an XXXXXX elevation of 40 cm, and its flash point is 190°. The explosive properties of tetryl may be characterized as follows: temperature of explosion 1100 kcal/kg; volume of gaseous explosion product 765 ltr/kg, work performed in Trauzl block 340 cc, brisance 19 mm due to these, velocity of detonation (at 1.63 density) 7500 m/sec. Tetryl

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is more susceptible to detonation than trotyl. The maximum initiating charge

of mercury fulminate for pressed tetryl is 0.29 gm, and for lead azide is 0.03 gm.

Tetryl is employed primarily to make detonators, booster charges for combined

capsules and detonators, and in detonating fuses, and occasionally as a bursting

charge in small-caliber shells, sometimes in the ~~phlegmatized~~ phlegmatized form.

Section 2. <u>Technology of Tetryl Production</u>

                Tetryl
a) <u>Production of ~~Tetryl~~ from Dimethylaniline</u>

The technological process for the production of tetryl includes the following

stages:

1) Production of dimethylaniline sulfate;

2) Nitration of dimethylaniline sulfate;

3) Processing of the tetryl, consisting of washing and crystallization;

4) Recovery of the mother solvents;

5) Drying of the tetryl.

~~Table~~ Figure 65 illustrates the process of tetryl manufacture (Bibl.16).

<u>Production ~~and~~ of dimethylaniline sulfate</u>. Dimethylaniline is gradually

(over a period of 50 - 60 min) run into a neutralizer (3), at 35 - 45°, into which

commercial sulfuric acid has first been run. When run-in is completed, it is

held (15 min) at ~~XXXXX~~ 45 - 50°, and a sample for analysis is taken.

The solution of ~~XXXXX~~ dimethylaniline sulfate should be a homogeneous

transparent liquid, brown in color, and having the specific gravity of 1.68 - 1.70.

The total acidity of the ~~XX~~ solution fluctuates in the range of 83 - 84%. The

composition of the solution of the dimethylaniline sulfate is (in %):

H_2SO_4 (monohydrate) . . . . 83.0 – 83.8

Dimethylaniline sulfate   . . . . 10.4 – 10.5

Water   . . . . 5.8 – 7.1

Nitration of dimethylaniline sulfate. A sulfate solution of dimethylaniline

sulfate is added slowly to the nitrator (7), filled with melange and heated to

40 – 45°. The rate of run-in should guarantee that the temperature will rise

to 50° in the first 5 min, and to 60° thereafter (1 – 1.5 hrs). The temperature

of the nitro mixture is regulated by the rate of run-in and cooling.

Upon conclusion of run-in, the mixture is held for 10 min at 58 – 60°,

whereupon the resultant tetryl is monitored in terms of its color (against a control

color scale). Tetryl, wetted with water, should be bright ЖХ yellow. If the color

product is dark yellow or reddish color this means that the nitration process has

not been completed and the mixture must be held for an additional period, with

the addition of a little more melange to the nitrator.

run-in period,
At the end of the sulfate ЖЖХХИХ foam is formed because of the abundant

liberation of gaseous ЖХ products of oxidation. During the holding time, formation

of foam gradually ceases. If foaming is particularly abundant, the charging of

the salt must be stopped and a careful observation of temperature must be

maintained, so that it does not rise above the permitted limit. Sometimes, if

foaming is strong, it is useful to add a little melange. This reduces the

viscosity of the mixture and facilitates removal of gases.

455
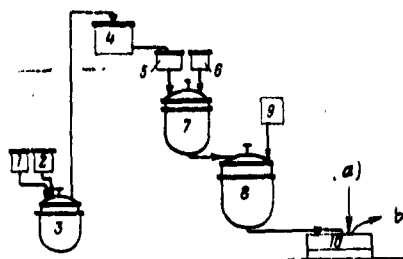
Fig.65 - Diagram of Production of Tetryl from Dimethylaniline (DMA)

1 - Commercial sulfuric acid metering tank; 2 - Dimethylaniline metering tank;

3 - Neutralizer; 4 - Sulfate salt collector; 5 - Sulfate salt metering tank;
Diluter;
6 - Melange metering tank; 7 - nitrator; 8 - ~~DILUTER~~ 9 - Water tank; 10 - Filter

and hopper

a) Water; b) Tetryl to washing

At the end of nitration, the nitrator contents are ~~run~~ run into diluter (8),

half filled with water. Dilution is performed with intensive mixing, and

temperature not over 50°.

Treatment of the tetryl. The dilute nitro mass is discharged ~~XXX~~ to the

filter-hopper, where the tetryl is separated from the spent acid and washed with

cold water. After washing, the tetryl contains 0.5 - 1% residual acid, while the

tetryl going to recrystallization should contain, upon recrystallization from

benzene, not more than 0.15% acid, whereas ~~XX~~ upon recrystallization with acetone

it contained not more than 0.11% acid. The required acidity may be attained by
cold
increasing the number of washings with/water (to 6 - 7); however, after this, the

tetryl has a low freezing point, and it is therefore treated several times ~~IN VATS~~

in vats of boiling water.

At identical acidity, the freezing point of tetryl will differ very sharply,

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depending upon the method of washing. The mean increase in freezing point after boiling at 1.4° (from 126.0 to 127.4°). In the process of washing tetryl with hot water, and boiling, not only are the mineral acids removed, but the organic acid impurities, which reduce the temperature at which tetryl freezes. Tetryl washed only with cold water cannot be recrystallized, as under these conditions the solvent is rapidly saturated with impurities, and partial replacement is required.

In order to accelerate the washing of tetryl, the traces of acids and other impurities in tetryl are removed by cooking in dilute soda solutions, at certain plants in the United States.

In technical tetryl, the following impurities are found after washing with water: dinitromonomethylaniline; tetranitrophenylmethylnitroamine (meta-nitrotetryl); products of the resinification of dimethylaniline, as well as of monomethylaniline, which are always present in technical dimethylaniline; inorganic acids; mineral salts and mechanical impurities carried into the tetryl with the acids and wash water; products of hydrolysis of tetryl and meta-nitrotetryl.

The product of the lower degrees of nitration of dimethylaniline, and the product of resinification reduce the susceptibility of tetryl to detonation, and its brisance. The products of the higher degrees of nitration result in reduced chemical stability of the tetryl. (The uncrystallized tetryl will stand/an Abel test for a few minutes, whereas tetryl recrystallized from solvent will stand it for tens of minutes).

The presence of mechanical impurities that have entered as a consequence of

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corrosion of the apparatus or inadequate purification of the water entering

for washing increases sensitivity to mechanical effects, which also makes for the

need for further purification of tetryl by recrystallization.

Of the large number of solvents in which tetryl is soluble to a greater or

lesser degree, only acetone, benzene, and nitric acid are of practical value.

Acetone is the best solvent. Tetryl crystallized from acetone has a high

solidification point and forms crystals of spicular form, which flow rather freely

and are therefore convenient for the filling of detonator caps. Crystallization

from benzene yields tetryl having a somewhat

lower freezing point. A product is obtained

in the form of small crystals and flows

poorly, making it difficult to use if for

filling. However, this method makes it

possible to wash tetryl in solution and

is therefore employed in industry (Bibl.16).
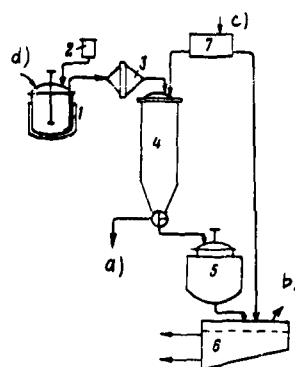
Fig.66 - Diagram of Recrystallization
of Tetryl from Benzene

1 - Solvent; 2 - Benzene metering tank;

3 - Filter; 4 - Washing apparatus;

5 - Crystallizer; 6 - Vacuum hopper;

7 - Hot water tank

a) Wash water; b) Tetryl to drying;

c) Steam; d) Tetryl

Desvergnes (Bibl.15) has described the

purification of tetryl with nitric acid.

He has demonstrated the good solubility

of tetryl in nitric acid and its suitability

purposes of

for recrystallization of tetryl.

A significant shortcoming of this method is the difficulty involved in the subsequent

the
washing of/tetryl free of nitric acid.

Recrystallization of tetryl from benzene is illustrated in the diagram in

Fig.66 (Bibl.16).

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The benzene is run into solvent (1) from metering tank (2), and raw tetryl is charged in. At the conclusion of the charging period the contents of the dissolving unit are heated, with stirring, to 65 - 70°, and held until the tetryl has dissolved completely. The solution obtained is forced through filter (3) and washing apparatus (4), to which hot water is added. The washed tetryl solution is lowered into crystallizer (5), which has first been heated to 30 - 35° to avoid the formation of a crust of crystals on the cold parts of the apparatus. After charging and stirring of the solution for 10 min at 65 - 68°, it is cooled, with a slow reduction in temperature to 15 - 20° (in a 3 - 4 hr period).

When crystallization has come to completion, the crystallizer contents are discharged to the vacuum hopper (6), with agitator working. The tetryl is separated out and washed once or twice with benzene. The mother benzene is used several times. From the vacuum hopper, the tetryl is unloaded into sacks and sent to drying. The tetryl crust formed on the walls of the crystallizer is removed with the mother solvent at 70 - 75°.

240   A special feature of the crystallization of tetryl out of acetone is the impossibility of performing aqueous washing of the solution, as a consequence of which removal of the acid impurities from the solution of tetryl in acetone is ~~FXIXXXX~~ ruled out. When the mother liquor is used repeatedly, the acidity both of the tetryl and of the solvent increases sharply. As early as the second cycling of the mother acetone, the acidity of the tetryl prior to washing with alcohol (on the vacuum-hopper) exceeds 0.020%. After 12 - 13 cycles of the mother liquor, the acidity of the tetryl rises to 0.090 - 0.100%, and the acidity of the mother acetone ~~achieves~~ reaches 1%. Therefore, the care with which the mother

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acetone is separated from the crystallized tetryl is even more important in
this situation $\overset{\text{to}}{\text{to}}$ the quality of the final product than upon crystallization
from benzene. Particularly great is the effect of the residual unremoved mother
acetone upon the acidity of the tetryl. Removal of acid impurities from the
tetryl ~~KUULKKK~~ was achieved by careful centrifuging of the mother acetone, as
well as by the use of crystalline tetryl alcohol for washing.

Crystallization
~~EKYKXXIXXKKKK~~   of tetryl out of acetone is performed as follows.

The tetryl is first dried to a moisture content of not more than 0.4%
(if moist tetryl is to be crystallized, the quantity of acetone is ~~KK~~ sharply
increased). Pure acetone (or mother acetone with pure acetone added) and tetryl
are charged into the solvent. One part tetryl by weight is charged in per part
pure acetone by weight. When mother acetone is employed, 1.4 part mother ~~KKIKX~~
acetone is charged per part tetryl by weight .

Upon conclusion of the charging, the contents of the dissolving units are
heated (with stirring) to 57 - 2°, and held for 20 min, subsequent to which
the filter is driven from the solvent into a crystallizer. In the crystallizer,
(over
the solution is slowly cooled ~~KKK~~/a 3 - 3.5 hr period, with stirring) to
15 - 20°, whereupon the crystallizer contents ~~KK~~ are delivered to the vacuum-hopper
to centrifuge the mother solvent. After careful removal of mother acetone, the
crystallized tetryl is washed on a vacuum-hopper with alcohol, centrifuged to
~~KKKKXXXXX~~ separate from the alcohol-acetone mixture, and sent to drying.

The mother solution may be used as many as 13 times in the ~~KX~~ crystallization
process, and is then redistilled after it has become saturated with impurities.

Recovery of mother solvents. After being employed through many cycles,

the mother solvents become saturated with impurities, from which they

are cleansed by distillation. To do this, the mother benzene is placed in the

distillation still, and is heated with spent steam to $55 - 60^{\circ}$. At this

temperature, live steam is fed into the still. The water vapors and benzene

rectifier
pass through a deflegmator to a condenser, where they are condensed

and collected in a receiver. The distilled benzene is returned to the tetryl

crystallization cycle. The still residues are cooled, drained to the

vacuum-hopper, centrifuged free of water, and sent to be burned. Before distillation

of the mother acetone, it is diluted with water through concentration of $40 - 45\%$.

The mass is stirred for 40 min, and then discharged into the vacuum centrifuge.

The centrifuge tetryl is subjected to recrystallization. The filtered,

diluted acetone is charged into a still and heated with spent steam. The

rectifier
acetone fumes go through a deflegmator and condenser. In the $62 - 70^{\circ}$ temperature

interval, the first fraction, consisting of acetone at a concentration of more

than 92%, is taken off. This acetone is reused as a solvent in the crystallization

of tetryl. The second fraction, consisting of $50 - 55\%$ acetone, which is then

redistilled, is taken off in the $70 - 90^{\circ}$ interval. The still residues are

centrifuged free of water and sent to be burned.

241   Drying the tetryl. The drying of crystallized tetryl is performed in

rack-type dryers or in vacuum desiccators. Tetryl crystallized

out of benzene is dried at $60 - 65^{\circ}$ for $24 - 32$ hrs, and, if crystallized out of

acetone, the temperature is 75° and the time $14 - 18$ hrs. Upon completion of

drying, tetryl is sent through a No.10 sieve, packed, and made up into lots.

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The tetryl has to satisfy the following specifications (Bibl.16):

- Appearance - crystalline powder with no mechanical impurities visible

to the eye;

- Color - bright yellow, and homogeneous throughout. For tetryl obtained

upon crystallization from benzene, a yellow color is permissible;

- Freezing point, ^{o}C - not less than 127.7;

- Temperature and volatile substances in $\%$ - not more than ~~EXIX~~ 0.02;

- Impurities insoluble in acetone in $\%$ - not more than 0.1;

- Total acidity, in terms of H_2SO_4 in $\%$ - not more than 0.01.

Types of tetryl rejects: a) rejects due to freezing temperature are corrected

by washing on the vacuum-hopper with benzene or acetone, or by ~~XF~~ recrystallization;

b) rejects due to acidity are corrected by washing with hot distilled water on

the vacuum-hopper; c) rejects due to color (green tetryl) cannot be corrected, and

the product is burned.

b) <u>Production of Tetryl from Chlorobenzene and Methylamine (Bibl.16, 27, 28, 29,30)</u>

The production of tetryl from chlorobenzene and ~~MMXYX~~ methylamine consists of

the following processes: production of dinitrochlorobenzene, production of ~~dXKIXFKMKX~~

dinitromonomethylaniline, and production of tetryl. The first two processes were

performed, in Germany, where this was the method used in World War II, at plants

manufacturing ~~XMXMMMXIXIMM~~ dye ~~XMXM~~ intermediates, and the latter process - nitration

of dinitromonomethylaniline - was performed at an explosives plant.

The production of dinitrochlorobenzene has been described previously (see p.201).

Dinitromonomethylaniline is ~~XMX~~ obtained by condensation of dinitrochlorobenzene

with methylamine in aqueous solution.

~~MMX~~

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241   Methylamine may be produced by IX heating a mixture of ammonium chloride and

formalin at 105 - 108° XXXX for 2.5 hrs, with consequent formation of CH_3NH_2 · HCl

(Pibl.20).

The
XXXXX condensation reaction is run in the presence of caustic alkali at 65 - 70°.

The resultant product, having a freezing point of 170 - 172° and a moisture of 10%

is sent explosives plant for nitration to tetryl.

Figure 67 illustrates the production of tetryl from dinitromonomethylaniline.

For safe nitration, dinitromonomethylaniline is converted to the sulfate salt.

With this object, dinitromonomethylaniline is introduced into agitator (2), containing

2.5 times its quantity in sulfuric acid (96 - 98% H_2SO_4). The solution of the sulfate

salt in sulfuric acid is delivered, simultaneously with the nitro mixture, into the major,

continuous XXXXXX nitrator (6). The temperature in the major nitrator is held at 40°,

and the buffer nitrator 20°.

From the buffer nitrator (7), the reaction mixture goes, in sequence, to two vacuum

hoppers (9). At the center of the vacuum hopper there is a discharge aperture with a

cover atop it. Vacuum is employed to centrifuge the spent acid out of the vacuum hopper,

and the tetryl is washed out with water through the central aperture into one of two

agitators (10), with stirrers and a conical bottom. Here, the precipitate is mixed with

water and the suspension is sent to vacuum-centrifuges (11), where the residue is
                                                                          soda
centrifuged free of water and washed, first with XXXXX solution, and then with water.

The spent acid contains approximately 60% H_2SO_4 and 7% HNO_3.

242   The raw tetryl is sent to recrystallization in another building. The recrystallizatic

procedure is illustrated in Fig.68.

XXXXXXXXXXXXXXXXXX(X)XXXXXXXXXXXXXXXXXXXXXXXXXXX

Two hundred liters of water are run into crystallizer (1), of stainless steel, from tank (7); 80 - 90 liters of acetone are run into tank (2), and the raw tetryl is run into tank (3) (onto a sieve at its bottom). The acetone from tani (2) is drained into crystallizer (1) (over the water) and heated to boiling. The acetone vapors are sent to condenser (4) from which the condensate is discharged to a tank (3), where the acetone dissolves tetryl, and the solution flows to a crystallizer. After solution of
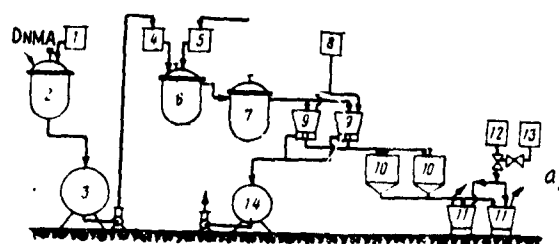

Fig. 67 - Diagram of Production of Tetryl from Dinitromonomethylaniline (DNMA)
1- Commercial sulfuric acid metering tank; 2 and 10 - Agitators; 3 - Sulfate receiver; 4 - Sulfate metering tank; 5 - Mixed-acid metering tank; 6 - Main nitrator; 7 - Buffer nitrator; 8 and 12 - Water tanks; 9 and 11 - Vacuum filters; 13 - Tank for МИ soda solution; 14 - Spent acid collector
a) Tetryl to crystallization

all the tetryl, which occurs in about 3.5 hrs, the acetone is sent from the condenser to tank (2), and heating is continued until it is completely driven out of the crystallizer. The contents of the crystallizer are then cooled to 20°. The driving off and cooling take about 1.5 - 2 hrs. Then, a little soda is added to the crystallizer (1), and the mass is sent to a vacuum filter (5) where the tetryl is filtered off. The filtered water from receiver (6) is sent to tank (7) and reused. The filtered and washed tetryl is dried at 70° over a period of 15 - 18 hrs.

The melting point of the product is 129.5°.

Safety. Tetryl manufacture is dangerous. XXXXXXXXXXXXXX

The nitration of dimethylaniline sulfate is accompanied by the considerable heat

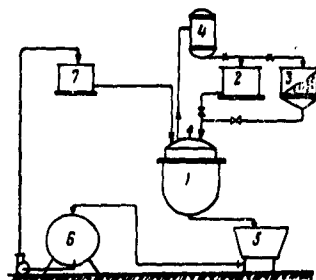effect. A sudden rise in temperature due to cessation in agitation or cooling will

Fig.68 - Diagram of Recrystallization
of Tetryl from Acetone
1 - Crystallizer; 2 - Tank for
acetone; 3 - Tank for tetryl;
4 - Condenser; 5 - Vacuum filter;
6 - Receiver for water; 7 - Tank
            for water

usually terminate in the expulsion of the

mixture from the nitrator, and in its ignition.

Should the temperature drop, the rate of nitration

is sharply reduced, and the conditions arise for

sudden development of an exothermic reaction

(due to accumulation of unreacted components),

which often terminates in ignition of the mass.

Prevention of these phenomena requires that

acceleration of run-in of components to the

nitrator to a speed inducing a rise in temperature

above the permissible level be prohibited. It is

necessary to maintain a proper relationship

243   among the components delivered into the nitrator. If the temperature rise is greater

XXXXthan that established in terms of a technical process, run-in has to be stopped XXXXXXXXXX

immediately, and cooling intensified. If these measures do not suffice to stop the

rising temperature, it is necessary immediately to dump the nitrator contents into an

emergency vat already full of water. -

The nitration shop must have good ventilation of the processes, inasmuch as a large

quantity of dangerous gases (nitrogen oxides, XXXXXXXX dimethylaniline fumes) is

liberated in the course of the work.

Unpurified raw tetryl has little XXX stability. Among other things, this renders

difficult nitration in continuous-action apparatus. Whereas, in XXXX batch-type work,

the nitrator, and the other apparatus are carefully washed free of products after each

operation, in continuous apparatus, some portion of the tetryl will be retained for a

considerable period on such portions of the apparatus as the coils, the upper portion

of the inner surface of the nitrator, the cover, etc. In the course of time, this

product will decompose and may even ignite. Thus far, periodic stoppage of

continuous-action systems for washing and cleansing of all apparatus continues to be

a realistic method of combating this phenomenon.

The process of crystallization of tetryl is also dangerous, and it particularly

pertains to crystallization out of acetone, which is highly combustible and may create

explosive mixtures with air.

Before repair, it is necessary to clean and wash the apparatus carefully. The

possibility of flame must be eliminated completely in the shop, and therefore there

must be dependable insulation of wires. Motors must be installed in a different building,

and illumination should be from without.

Section 3. Tetryl Analogs

2,4,6-Trinitroaniline (picramide)
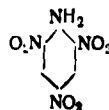
is a XXXX hygroscopic crystalline substance, yellow in color, with a melting point of

192 - 195°.

Production of trinitroaniline begins with ortho- or para-nitroaniline, which is

dissolved in 10 parts 95% XXX sulfuric acid by weight and then nitrated with a mixture

consisting of 1.5 part potassium nitrate by weight, and 10 parts 95% sulfuric acid.

243   Nitration is performed at a temperature of 0 – 5°. When run-in is completed, the mass

is left until the next day and then 4.5 ltr saturated table salt solution is added at 0°.

The picramide comes down as fine crystals. It is centrifuged out and washed with

water. The yield of product is about 80% of the theoretical. The low yield is due

to partial hydrolysis of the product, in the course of which ammonia and picric acid,

which are comparatively readily soluble in water, are formed:

$$C_6H_2(NO_2)_3NH_2 + H_2O \rightarrow C_6H_2(NO_2)_3OH + NH_3.$$
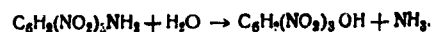
Picramide may also be obtained from aniline by ~~XXX~~ preliminary conversion thereof

into acetanilide $C_6H_5NH-COCH_3$, in the nitration of which the metanitro derivative is

not obtained as occurs in the nitration of aniline in sulfuric acid solution.

The explosive properties of picramide are: volume of gaseous explosion products

724 ltr/kg, heat of explosion 990 cal/kg, Trauzl block expansion 296 cc.

                                      trinitroanisole
Trinitroaniline approximates ~~XXXXXXXXXXXXX~~ as an explosive, but is considerably

inferior to tetryl (Ritl.30). Picramide has no practical application at the present

time.

244   2,3,4,6-Tetranitroaniline
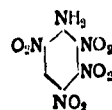
is a yellow crystalline product which decomposes upon fusion at 217 – 220°, and has a

specific gravity of 1.867. A density of 1.68 is attainable by pressing. ~~XXXXXXXXX~~

Tetranitroaniline is virtually non-hygroscopic, insoluble in water, and poorly soluble

in the common solvents, and can be recrystallized from nitroxylene.

At room temperature, water virtually fails to react with tetranitroaniline, but

at 50°, the reaction goes at a noticeable velocity, while upon boiling, conversion into

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trinitroaminophenol goes quite energetically:
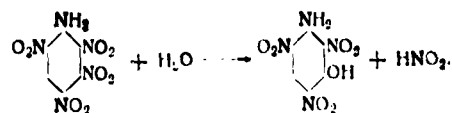
Heating with ethyl alcohol results in the formation of trinitroaminophenetol. The nitro group in the meta-position is instantaneously and completely detached at room temperature in an aqueous acetone solution of sodium acetate, also resulting in the formation of trinitroaminophenol. When KOH is reacted with trinitroaminophenol, trinitroresorcinol is formed:
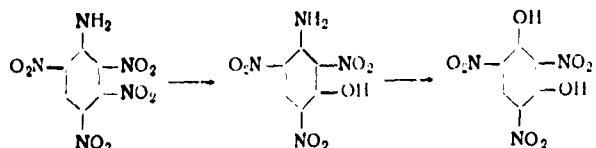
The stability of tetranitroaniline is satisfactory. It will stand an Abel test at 71° for 1 hr. The tetranitroaniline manufactured during World War I was no longer useful after 9 years and further storage was dangerous.

The flash point is 222 - 223°. The shock sensitivity is considerably less than that of tetryl. Expansion in a Trauzl block is 430 cc, i.e. 10 - 15% higher than that of tetryl.

According to A.A.Solonina who made a detailed study of the properties of tetranitroaniline, it may serve as a substitute for tetryl (Bibl.23). A plant to manufacture tetranitroaniline for use in filling detonators was built in the USA during World War I.

According to the Flurscheim patent, tetranitroaniline is obtained from meta-nitroaniline by solution of 1 part thereof by weight in a mixture consisting of 3 parts KNO_3 by weight and 36 parts commercial sulfuric acid by weight at 68 - 70°.

After the mixing of the components, the mass is held at a temperature of 100°. Then, (upon completion of the reaction), it is cooled to 20°, and the product is filtered. The product yield is 70% of the theoretical.

A.A.Solonina nitrated with nitric acid, having first dissolved the metanitroaniline in commercial sulfuric XIX acid.

Nitration of the meta-nitroaniline with mixed acid goes through the stage of formation of nitrophenyl-N-nitroamine, which is then prearranged with dinitroaniline (Bibl.31):
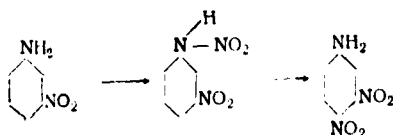
2,3,4,6-Tetranitrophenylmethyl-N-nitroamine (meta-nitrotetryl)
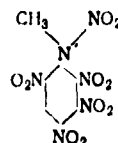
was first obtained by van Romburgh in 1889 (Bibl.12) by dissolving dimethylaniline (1 part by weight) in commercial sulfuric acid (37 parts by weight) and then by pouring a mixture consisting of nitric XXX acid (1.2 parts by weight 89.6% HNO_3) and commercial sulfuric acid (6 parts by weight) into the mixture cooled to -2°. The temperature during the run-in has to be -2°. The mixture is held at that temperature after the acid is run in. Under these conditions, it is chiefly meta- and para-nitrodimethylaniline) that is formed. The large amount (37 times as much) of concentrated sulfuric acid facilitates an increase in the yield of meta-isomer, from which meta-nitrotetryl is obtained.

The solution resulting after holding is run into nitric acid (22.5 parts 89.6% HNO_3

by weight) and held for a week. The meta-nitrotetryl which forms crystallizes out of

solution, and the tetryl obtained simultaneously remains in the mother liquor.

The meta-nitrotetryl that has come down is separated from the solution, washed with

water, and dried.

As already indicated above, meta-nitrotetryl can be obtained XX under other

conditions by the nitration of dimethylanilinesulfate (the conditions for production

of tetryl). However, the main source of the formation thereof in this latter case is

deemed to be an admixture of monomethylaniline in the initial dimethylaniline.
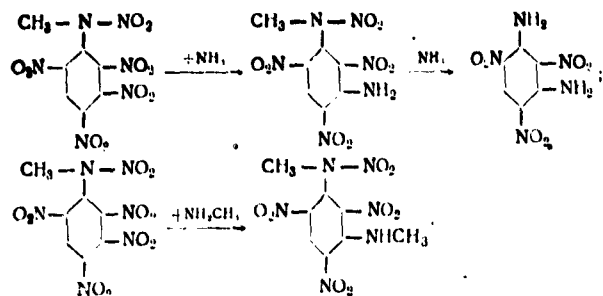
Meta-nitrotetryl is a white XX crystalline substance with a yellowish tinge, having

a melting point of 146°.

The nitro group in the meta-position is readily replaced by hydroxyl when the

material is treated with water. In treatment with soda, both the nitro group in the

meta-position and the nitro amine group undergo saponification, the consequence being

a double sodium salt of styphnic acid:
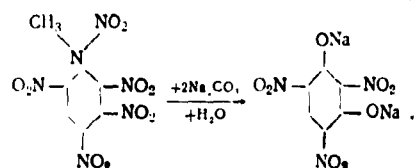
Analogous reactions also occur under the effect of other reactants (Bibl.32):
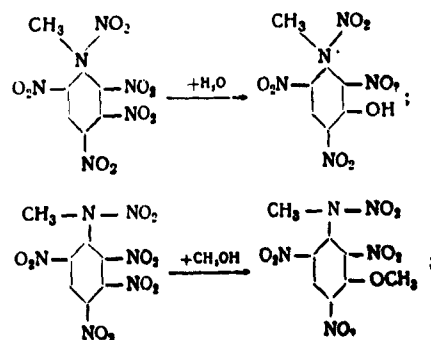
The reaction product of meta-nitrotetryl and water – XXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

trinitrooxyphenylmethylnitroamine is a colorless crystalline substance with a melting

point of 187°. It is readily soluble in water, alcohol, benzene and ether. The

presence of three nitro groups in the trinitrooxyphenylmethylnitroamine ring causes the

hydrogen atom of XXXXX the hydroxyl group to acquire acid characteristics. Upon reaction

with metals, trinitrooxyphenylmethylnitroamine forms salts. Specifically, upon reaction

with iron, it forms an iron salt in the form of a crystalline dark brown powder readily

soluble in XX water, acetone, and alcohol, and XXXXXXX insoluble in benzene, ether,

and carbontetrachloride. When crystals of this salt are heated slowly, they carbonize

without melting, and when they are heated rapidly they flash.

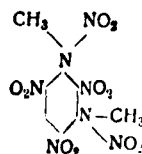2,4,6-Trinitro-3-methylphenylmethyl-N-nitroamine (methyltetryl)
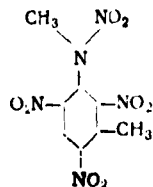
is a crystalline substance melting at 101°. It was first obtained by van Romburgh in

1876 (Bibl.33) by the nitration of dimethyl-meta-toluidine. Davis (Bibl.34) obtained

it from the sodium salt XXXXXX of dinitrotoluenesulfonic acid:
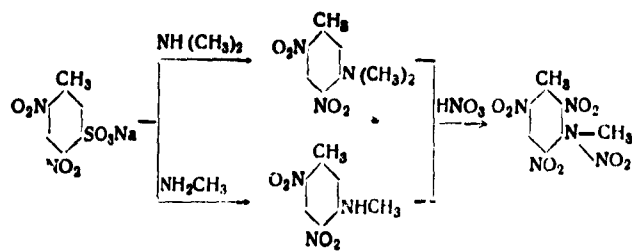
An analogous process was developed by T.Urbanski (Bibl.16).

Methyltetryl may also be obtained from the 和政XIX wastes of trotyl production:

sulfite caustics (see section "Trotyl Production").

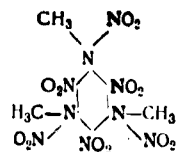2,4,6-Trinitro-1,3-di-(methyl-N-nitroamino)-benzene (ditetryl)

247 (or, more accurately, methyl-N-nitroaminotetryl) is a crystalline substance melting at

206°. It was first obtained by van Romburgh in 1887 (Bibl.35) by nitration of

N,N'-dimethyl-meta-phenylenediamine. A more convenient method is that of obtaining

it from tetranitromethyl-N-nitroamine, as developed by van Duyn (Bibl.32):
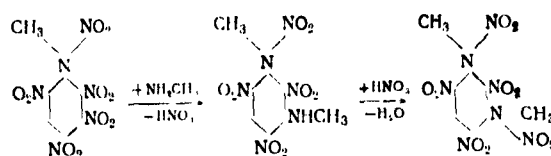
In its explosive properties, this substance is virtually equivalent to tetryl.

However, it is more sensitive to mechanical effects. Ditetryl explodes when a 2 kg

weight is dropped from 21 - 26 cm (for tetryl a height of 49 - 51 cm is required)

(Bibl.16). The flash point of ditetryl is 214°.

2,4,6-Trinitro-1,3,5-tri-(methyl-N-nitroamino)-benzene

$$CH_3 \quad NO_2$$

Tritetryl, or, more accurately, dimethyl-N-nitroamino-tetryl is a crystallized

substance with a melting point of 280° (melts with decomposition). It was first

obtained by Blanksma in 1908 (Bibl.36) by nitration of 2,4,6-trinitro-1,3,5-

trimethylaminobenzene. In 1937, T.Urbanski (Bibl.37) suggested a method of producing

tritetryl from trinitrotrichlorobenzene:
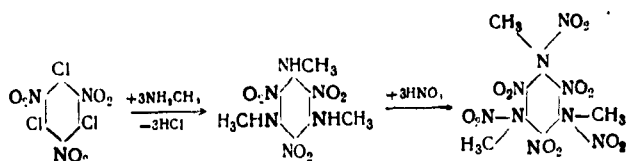
He also was responsible for determining the explosive properties of this product

and showed that tritetryl is similar to tetryl.

Thus, despite the fact that the molecule of this substance has six nitro groups,

as against four in the case of tetryl, no greater explosive property is observed.

2,4,6-Trinitrophenylethyl-N-nitroamine (ethyltetryl)
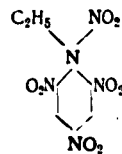
is a crystalline substance with a melting point of 96°. It was first obtained by

van Romburgh in 1883 (Bibl.33) by nitration of ethylaniline. In its properties, this

product is similar to tetryl (its explosive characteristics are somewhat lower). Medard

(Bibl.38) showed the fugacity of ethyltetryl to be 1.04 times that of picric acid.

Ethyltetryl may be produced by condensation of dinitrochlorobenzene with

monoethylamine and subsequent nitration of the dinitro compound obtained by mixed

sulfuric and nitric acid (50 - 60% H_2SO_4 and 40 - 50% HNO_3) at 40 - 50° (Bibl.39).

Section 4. **Hexanitrodiphenylamine (Hexyl)**

Hexanitrodiphenylamine

was first obtained by
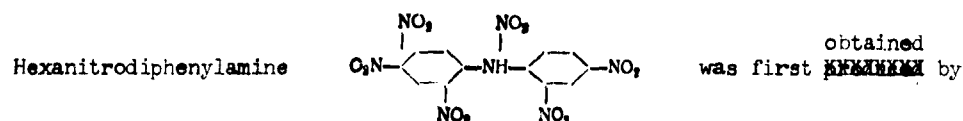
Austen in 1874 by nitration of picril-para-nitroaniline:
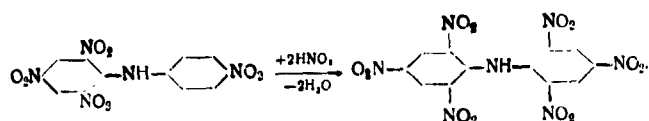
Gnehm obtained it by nitration of diphenylamine. These methods have not found

practical application because of the high cost of the hexyl.

In 1913, Carter worked out the method that has found practical application, based

on reaction of 2,4-dinitrochlorobenzene with aniline, resulting in dinitrodiphenylamine:
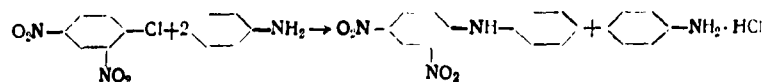
Nitration of this product with nitric acid yields hexyl. The production of hexyl

was begun in Germany in 1915, with the use of this method.

In 1920, Marshall in the USA suggested that hexyl be produced by treatment of

dinitrodiphenylamine with mixed sulfuric and nitric acid.

Properties of hexyl. Hexyl is a yellow crystalline powder with a melting point

of 245° (and it decomposes on melting).

Hexyl is not soluble in the usual solvents or in water. It hygroscopicity is

0.09%. It is capable of being recrystallized from acetone, glacial acetic, and

concentrated nitric acids.

Because of the presence of six nitro groups, the hydrogen atom in the amino group

is acid in character, and this is expressed in the fact that it is capable of being

replaced by a metal, i.e., hexyl behaves as an acid КИК (Bibl.40, 41). Metallic salts

thereof may be obtained by heating aqueous or alcohol КАIНХIАКI solutions of metal

hydroxides or carbonates with hexyl suspended in these solutions. The metal salts

are, except for the ammonia МАX and magnesium salts, XX more sensitive to mechanical

effects than is hexyl. The lead salt is the most sensitive. However, in view of the

fact that hexyl is virtually IХМАМ insoluble in water, the formation of salts is of

little probability under normal conditions.

Hexyl turns brown under solar КАМIХКIАК irradiation. Its stability is somewhat

less than that of trotyl, but higher than that of tetryl. The flash point is also

higher than that of tetryl, and is 250°. Shock sensitivity is less than that of tetryl,

but somewhat higher than that of picric acid. Hexyl is more sensitive to detonation

than tetryl. The maximum initiating charge (a mixture of mercury fulminate and

potassium chlorate) is 0.18 gm for hexyl, and 0.20 gm for tetryl. The volume of gaseous

explosion products is 675 ltr/kg, the heat of explosion is 1080 kcal/kg, the brisance $Ka\varepsilon t$

is 4.9 mm due to Kast, and the fugacity is 320 cc.. The velocity of detonation of

hexyl (at a density of 1.60) is 7145 m/sec.

The effect of hexyl upon the skin is to cause dermatitis. Hexyl dust irritates

the mucous membranes of the mouth and nose, and affects the lungs.

During the First World War, hexyl was employed with trotyl to fill naval munitions,

as a mixture of the following composition: 30 - 40% trotyl and 60 - 70% hexyl. The

density of these mixtures was 1.64 - 1.70. In the USA, the proposal was advanced that

hexyl be used for detonators instead of tetryl. During the Second World War, hexyl was

manufactured in some small quantity only in Germany, where it was employed in a mixture

with trotyl and aluminum to fill naval munitions (torpedoes and submarine mines). The

explosive properties of these mixtures are presented in Table 79.

Table 79

a)	b)	c)	d)	e)	f)	q)	h)
60/24/16	85	1,73	6840	610	1400	408	4,2
67/8/25	85	1,81	6600	468	1665	358	4,4

a) Mixture (trotyl-hexyl-aluminum); b) Temperature of filling, ^{o}C; c) Density, gm/cc; d) Velocity of detonation, m/sec; e) Volume of gases, ltr/kg; f) Heat of explosion, kcal/kg; g) Fugacity, cc; h) Brisance due to Kast, mm

Production of hexyl. Hexyl may be obtained by nitration of diphenylamine in one

or two stages. In the former instance, the diphenylamine is dissolved in sulfuric XX

acid, and the resultant solution is slowly run into concentrated nitric acid. In the

second case, nitration is run in two stages, the first employing a mixed acid consisting

of 60% HNO_3; 20% H_2SO_4; 20% H_2O, whereas the second stage uses a mixture consisting of

73% HNO_3; 25% H_2SO_4; 2% H_2O (Bibl.42).

When hexyl is produced on an industrial XX scale, the starting substances are

dinitrochlorobenzene and aniline, condensation of which yields dinitrodiphenylamine.

The resultant product is nitrated in two stages to hexyl.

in
These processes were developed XXXX Germany by Carter and in the USA by Marshall.

According to XXXXXXX Carter's method, alcohol is used as the medium for condensation

(2.5 parts alcohol by weight per part of dinitrochlorobenzene). Two moles of aniline

(1 mole going to neutralize HCl) is used per mole of dinitrochlorobenzene. Toward the

end of the reaction, the mass becomes thick and takes on a dark red color. Then, water

249   is added, neutralization with chalk is performed, and, ̶X̶X̶X̶X̶X̶X̶X̶X̶X̶X̶X̶ after filtration,

the mixture is washed with water. The result is dinitrodiphenylamine with a melting

point of 150 - 154° (the pure substance melts at 156 - 157°).

Nitration to tetranitrodiphenylamine is performed with 52% nitric acid (8 parts

by weight per part of product by weight). Delivery of the nitro product into the

nitric acid was begun at 40°, and ended at 90 - 100°. Upon cooling, the ̶X̶X̶X̶X̶X̶X

tetranitrodiphenylamine dissolved in the hot HNO_3 came down:
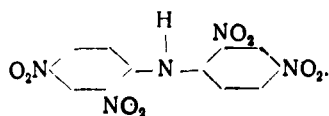
Nitration of the tetranitro product to hexyl is performed with 98% nitric acid

in ̶X̶X̶X̶X̶X̶X eight-fold the weight of the product. Mixture of the components begins at

                                                        suction filters.
40° and ends at 90°. Hexyl is separated from the spent acid on ̶N̶u̶t̶s̶c̶h̶e̶s̶. Washing of

the hexyl with water is also conducted in this equipment. After the washing, the hexyl

is centrifuged free of water and dried at 70° for 36 - 48 hrs.

Under Marshall's method, condensation is performed in water. Toward this end,

2 moles of aniline and 1 mole of dinitrochlorobenzene are suspended in water heated

to 60°, in three-fold the weight of the combined chemicals. The mixture is heated,

250   with continuous agitation, at 80°, for 1 hr. The dinitrodiphenylamine forms as large

clumps of red spicular crystals. For complete solution of the aniline hydrochloride,
the mass
is stirred for another half hour at 80°. The resultant dinitrodiphenylamine is

filtered, washed with dilute hydrochloric acid, then with water, and dried. The

resultant product has a melting point of 148 - 152°.

Nitration is performed with a mixture of sulfuric and nitric acids. One part

dinitrodiphenylamine is added, at 70°, to four parts mixed acid of the following

250 composition: 30 - 45% HNO₃ and 40 - 50% H₂SO₄. It is then held that 80 - 90°, at the

conclusion of which the mass is cooled and filtered. The result is an amorphous

substance of yellow-brown color, which is nitrated to hexanitro compound by mixed acid

consisting of 60% HNO₃ and 40% H₂SO₄, 3.75 parts mixed acid by weight being employed

per part tetranitro product by weight. Mixture of the components is performed at 70°,

and it is held at 90°. The product is filtered, washed, and dried. The hexyl obtained

has a melting point of 238.5 - 239.5°.

Depending upon the method of production, the hexyl may be loose, dense, or

finely crystalline.

B. Hexogen and Other Nitro Derivatives of the Heterocyclic Amines

Hexogen or cyclotrimethylenetrinitroamine, along with PTEN, is one of the most

powerful explosives used in minitions in World War II by all the warring countries.

The reason for this is its high brisance and the stability of hexogen, a relatively
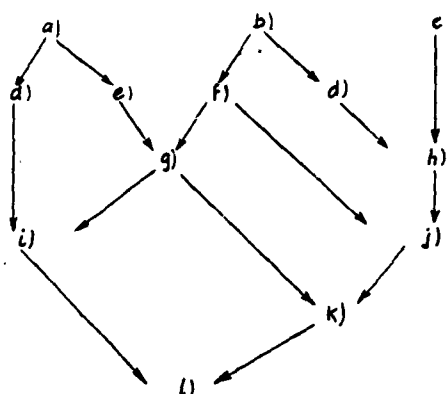

Fig.69 -

a) Air; b) Water; c) Coal; d) Oxygen; e) Nitrogen; f) Hydrogen; g) Ammonia (NH₃);

h) Carbon monoxide (CO); i) Nitric acid (HNO₃); j) Formaldehyde (CH₂O);

k) Urotropine [(CH₂)₆ N₄]; l) Hexogen [(CH₂NNO₂)₃]

250   simple production technology, and a virtually unlimited supply of raw materials,

inasmuch as the raw materials - urotropine and nitric XXX acid are ultimately

is
produced from coal, air, and water, as/shown in Fig.69.

Hexogen was first obtained in 1897 by Lenze. In 1899, Henning (Bibl.43) took

out a patent for a method of producing it via urotropinedinitrate, in the belief that

hexogen would necessarily have to have pharmaceutical properties. In 1920 Herz

(Bibl.44) suggested that hexogen be produced by direct nitration of urotropine with

concentrated nitric acid, and showed that it is an explosive. Since that XXX day,

investigations of methods of production of hexogen and study of its explosive properties

have continued.

251   As early as 1932 - 1933, production of hexogen by the Herz method in continuous-

process installations was begun in England (Bibl.45) and apparently in other XXXXX

countries as well. In subsequent years and, particularly during World War II, additional

methods of producing hexogen were developed.

The production of hexogen during World War II attained 360 tons per day in England

(Bibl.45),
XXXXXXXX 350 tons per day in the USA, 334 tons per day in Germany. During World War II

as a whole, Germany produced a total of 113,000 tons of hexogen (Bibl.46).

In Japan (Bibl.47), hexogen was employed in a mixture with trinitroanisole

XXXX (60% trinitroanisole and 40% hexogen). Hexogen was employed in mixtures with

other explosives in various types of munitions; artillery shells, aviation shells,

submarine mines, and torpedoes. The majority of ersatz explosives contained from
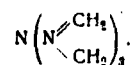
10 - 30% hexogen.

Section 1. <u>Chemistry of Production, Properties and Applications of Hexogen</u>

Hexogen may be obtained by nitrolysis of hexamethylenetetramine, or urotropine

$(C_6H_{12}N_4)$.

252   This last was ~~synthesized~~ by Butlerov in 1859. He believed urotropine to have

the following structure:

$$N\left(N{\overset{CH_2}{\underset{CH_2}{}}}\right)_3.$$

Later, Lozekan, proposed the following structure for urotropine, on the basis of

the structure of the product of reaction between urotropine and nitrogen oxides, which

proved to be dinitrosopentamethylenetetramine:

$$N{\begin{cases}CH_2-N=CH_2\\CH_2-N=CH_2,\\CH_2-N=CH_2,\end{cases}}$$
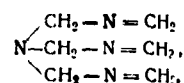
and that the reaction between urotropine and nitrogen oxides proceeded in accordance

with the following mechanism.(Pihl.48)

$$N{\begin{cases}CH_2-N=CH_2\\CH_2-N=CH_2\\CH_2-N=CH_2\end{cases}}\xrightarrow[-CH_2O]{+N_2O_3}\quad N{\begin{cases}CH_2-\overset{NO}{\underset{}{N}}-CH_2\\CH_2-N\\CH_2-\underset{NO}{\overset{}{N}}-CH_2\end{cases}}$$
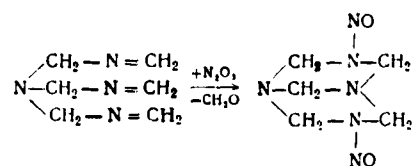
Duden and Scharf, like Lozekan, hold that all the nitrogen atoms in the urotropine

molecule are of the same type - trivalent, but that they are not in a single plane,

rather in the corners of a right tetrahedron:
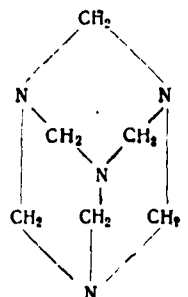
25⌐   This is confirmed by the reaction between urotropine and nitric acid, resulting in

the formation of trinitrosocyclotrimethylenetriamine:
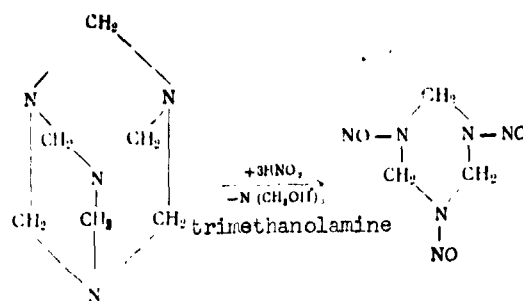
According to Bachman (Bibl.49,50), a medium of pH = 3 is required for the

formation of dinitrosopentamethylenetetramine, while a medium of pH = 1 is required

in order to obtain trinitrosocyclotrimethylenetriamine.

Studies of the structure of the crystal lattice of hexamethylenetetramine confirm

the correctness of the Duden and Sharf formula, by means of which one may arrive at

the structural formula of hexogen. Under these circumstances, hexogen may be regarded

as a derivative of a hypothetical cyclotrimethylenetriamine:
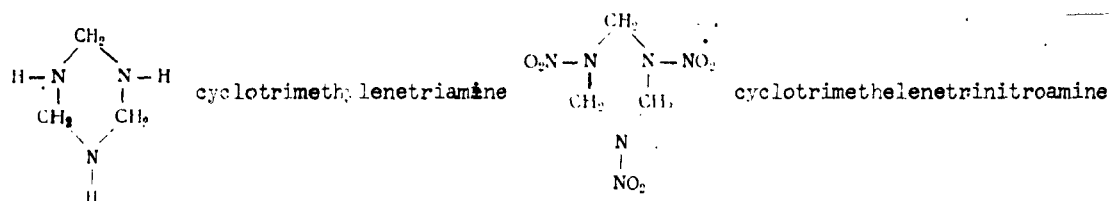
Urotropine is a white crystalline powder, sweet to the taste. It is stable upon

storage in air. When heated to over 100°, a small quantity volatilizes with partial

decomposition, and methylamine is formed. In vacuum, volatilization occurs at

230 - 270°, virtually without decomposition. The solubility of urotropine at 20° in

various solvents is adduced in Table 80.

Table 80

Solvent	Solubility of Urotropine, in gm, per 100 gm Solvent
Water	167
Absolute ethyl alcohol	2,89
90% ethyl alcohol	5,58
Benzene	0,23
Xylene	0,14

Urotropine is capable of reacting with hydrogen peroxide in the presence of citric acid, to form heamethylenetriperoxidediamine:

$$C_6H_{12}N_4 + 3H_2O_2 \rightarrow N{\overset{CH_2-O-O-CH_2}{\underset{CH_2-O-O-CH_2}{\overset{|}{-CH_2-O-O-CH_2-}}}}N + 2NH_3.$$
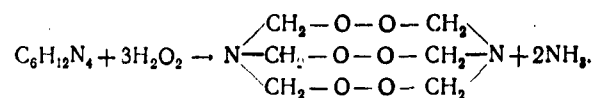
253

When an aqueous solution of sodium nitrite and sulfuric acid are reacted with hexamethylenetetramine, dinitrosopentamethyle tetramine КХХХХХХ is produced (Bibl.51):

$$ON-N{\overset{CH_2-N-CH_2}{\underset{CH_2-N-CH_2}{\overset{|}{\underset{|}{CH_2}}}}}N-NO,$$
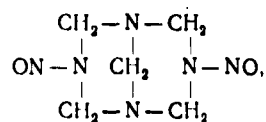
which is an unstable substance completely decomposable by water in accordance with the following mechanism:

$$C_5H_{10}N_6O_2 + 3H_2O \rightarrow 5CH_2O + 2NH_3 + 2N_2.$$
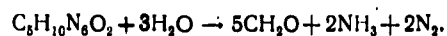
Urotropine is a weak base. With weak nitric and acetic acids, it forms salts, but sulfuric and hydrochloric acids decompose urotropine in accordance with the following equation

$$C_6H_{12}N_4 + 4H_2SO_4 + 6H_2O \rightarrow 6CH_2O + 4NH_4HSO_4.$$
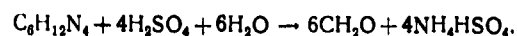
Acetic acid ХХХХХХ yields a salt of the following composition: $C_6H_{12}N_4 \cdot 3CH_3COOH$.

Nitric acid in the form of a weak alcoholic solution forms urotropine nitrate $C_6H_{12}N_4 \cdot HNO_3$, a crystalline substance readily soluble in water. An aqueous solution

thereof is neutral in reaction. When weak nitric acid (50%) reacts upon an aqueous XXXX solution of urotropine, urotropine dinitrate $C_6H_{12}N_4 \cdot 2HNO_3$ is formed.

Urotropine dinitrate may be obtained in two ways:

1) one part urotropine by weight is dissolved in 2 parts water; the solution is cooled to 0 - 5°, and 0.9 part 65% nitric acid by weight is added thereto gradually, with agitation;

2) dry urotropine, one part by weight per 2.5 parts acid is added gradually to 35% nitric acid, with agitation and cooling (to 5°).

In both cases, a white crystalline precipitate of urotropine dinitrate comes down out of solution. It is filtered and washed with a 50% aqueous solution of alcohol and ether. Yield is 95% of theoretical.

Urotropine dinitrate has a melting point of 165° (it decomposes on melting). It is readily soluble in water. As a consequence of hydrolysis, the solution acquires a highly acid reaction and, when allowed to stand, decomposes with liberation of formaldehyde. Urotropine dinitrate is not soluble in alcohol, ether, chloroform, XXXX acetone, and carbontetrachloride.

Urotropine dinitrate is an explosive, with a flash point of 190°, Trauzl block expansion of 190 cc, and a sensitivity to mechanical effects somewhat higher than that of trotyl.

The formation of urotropine dinitrate apparently occurs at all concentrations of nitric acid, and instantaneously, but in concentrated nitric acid it remains in solution, where it reacts with nitric acid, while in weak acid it crystallizes out of solution and leaves the zone of reaction.

Reaction of hexamethylenetetramine dinitrate and strong nitric acid at low

temperatures (-50 to -60°) results in the formation of 1,3-dinitro-1,3,5-triaza-n-pentane

nitrate

$$NO_2NH \cdot CH_2N(NO_2)CH_2 \cdot NH_2 \cdot HNO_3$$
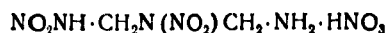
and of methylenedi-1(3,5-dinitro-1,3,5-triaza-cyclohexane) (HHX (Bibl.52)
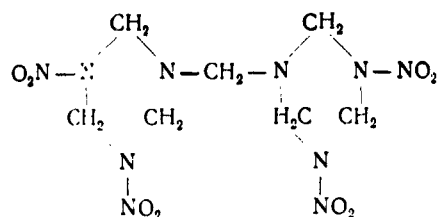
The solubility of the dinitrate in nitric acid depends upon the temperature and

the concentration of the acid. In 20% HNO$_3$, its solubility is minimal, but at lower

and higher concentrations of nitric acid, it increases. When the concentration of

HNO$_3$ is less than 10% and greater than 30%, the solubility of the dinitrate rises

sharply.

In air, urotropine dinitrate decomposes slowly, and the nitric acid disintegrates.

The HHX dinitrate is hygroscopic. Its crystals contain about 20% water. In the drying

of moist crystals, the nitric acid volatilizes along with the water of crystallization.

Desiccation (dehydration) of the crystals is performed in practice by washing them with

alcohol.

A higher yield of hexogen is attainable from urotropine dinitrate than from

urotropine. Moreover, the concentration of the nitric acid, the module, and the nitrogen

XI oxides content cf the HNO$_3$ has less of an effect upon the hexogen yield.

When urotropine is nitrolized to hexogen by concentrated nitric acid, 88 kcal/mole

of heat is emitted, but nitrolysis by the dinitrate is accompanied by the emission of

only 41.7 kcal/mole (Bibl.53).

Figure 70 illustrates the heat of reaction of XXXXIXXX nitrolysis of urotropine
and urotropine dinitrate with allowance for the heat of the side processes and of
hydration when nitric acid of various concentrations is employed for nitrolysis
(Bibl.54).
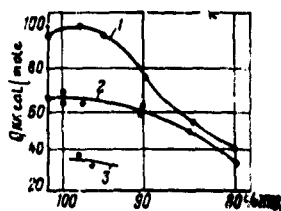
Fig.70 - Effect of Concentration of
Nitric Acid upon Heat of Nitrolysis
of Urotropine and Urotropine Dinitrate
(DNU) (with Allowance for Heat of Side
Processes and Hydration).
1 - Urotropine nitrolysis at 20°;
2 - Same at -35.5°; 3 - Urotropine
dinitrate nitrolysis at -35.5°
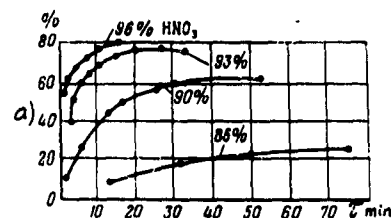
Fig.71 - Effect of Strength of Nitric
Acid upon Rate of Hexogen Formation
a) Hexogen yield

An important advantage enjoyed by urotropine dinitrate XXX intermediate product
for the production of hexogen is the fact that XXX it may be obtained not only from
urotropine, but also from formalin and ammonia, bypassing the stage involving separation
of urotropine from solution, and drying thereof. A method has also been suggested for
producing hexogen via urotropine dinitrate, in which the initial products are formalin,
ammonia, and nitric acid. However, it has not gained application because of the
solubility of urotropine dinitrate in water, and the inadequate stability.

Nitric acid, in 60 - 80% concentration, decomposes urotropine, and more concentrated acid converts it to hexogen. With increase in the HNO_3 concentration, the yield of hexogen increases (Fig.71) (Bibl.55). From this it follows that hexogen production requires the employment of nitric acid of not less than 93% concentration.

None of the velocity curves in Fig.71 reveal any period of induction. This demonstrates that the process rate is characterized by the speed of the nitrolysis reaction, and not by that of other processes.

The hexogen yield is significantly affected by nitrogen oxides, which give rise to oxidation of urotropine. If the nitric acid contains about 4% nitrogen oxides, the urotropine will burn out completely, and hexogen will not form at all. Therefore, nitric acid containing not more than 0.5% nitrogen oxides is employed for nitrolysis.

The optimum temperature of urotropine nitrolysis by nitric acid is 10 - 20°, and an increase therein makes for oxidizing processes and leads to a reduction in

25   the hexogen yield. The maximum yield when this reaction occurs is about 80%, in terms of urotropine.

A yield of 83% has been obtained by conducting the process very carefully and following the rate of urotropine addition (to eliminate local decomposition). The process was run with 21 moles 99.5 - 99.9% HNO_3 per 1 mole of urotropine at 20 - 25°, for more than 30 min. Upon completion of the mixing of the components, the reaction mixture was decanted into water (Bibl.49).

It has been established (Bibl.56) that the rate of nitrolysis of hexamethylenetetramine by nitric acid increases with increase in the modulus. Figure 72 illustrates the effect of the $-\dfrac{HNO_3}{C_6H_{12}N_4}$ ratio on the hexogen yield (Bibl.56). At all concentrations of nitric acid, up to 88%, maximum yields of hexogen (about 80%)

were attained on the condition that an adequate molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$ was adhered to.

The minimum molar ratio for maximum yield rises approximately from 26:1 with 97% acid XXXX to 110:1 with 88% acid.

If the molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$ is selected accordingly, one may obtain identical nitrolysis rate with nitric acids of various concentrations, as is evident from Fig.73, which shows the rate of hexogen formation at 0° and various concentrations of nitric acid.
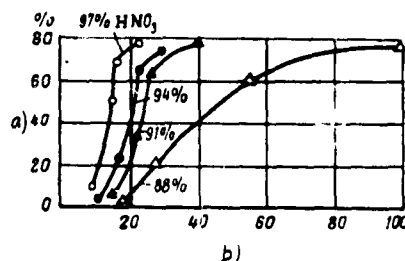
Fig.72 - Effect of $\frac{HNO_3}{C_6H_{12}N_4}$ Ratio upon Hexogen Yield

a) Hexogen yield; b) Molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$
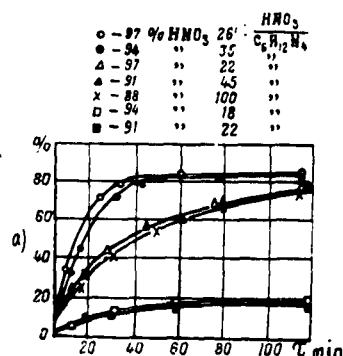
Fig.73 - Effect of $\frac{HNO_3}{C_6H_{12}N_4}$ Ratio upon Hexogen Formation Speed

a) Hexogen yield

At very large ratios $\frac{HNO_3}{C_6H_{12}N_4}$, the yield of hexogen is directly proportional to the amount of urotropine employed, and is not dependent upon the strength of the nitric acid (more than 88% HNO_3). Figure 74 illustrates this ratio, and it is assumed that one mole of hexogen is formed from three moles of HNO_3.

In practice, high molar ratios XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX $\frac{HNO_3}{C_6H_{12}N_4}$ rapidly increase the cost of hexogen, and therefore XXXX urotropine nitrolysis is performed at a molar ratio of 22 - 24, corresponding to 11 - 12 parts 98% nitric acid by weight per 1 part urotropine. This amount of nitric acid does not result in

maximum yield, but an increase therein by increase in nitric acid consumption

is economically undesirable.

On the basis of the fact that the maximum yield of hexogen is

achieved only with a large excess of nitric acid, and that this excess increases

sharply with reduction in the concentration of the acid, A.Vroom and C.Winkler

(Bibl.56) concluded that the concentration of the active nitrating agent in the

acid is not great and increases with reduction in the concentration of acid. These

writers hold that the active nitrating agent is the nitrate cation of

" nitrocidium", the $NO(OH)_2^{(+)}$ ion, formed from bimolecular HNO_3 in accordance with

equation

$$ON{\overset{O-H...O}{\underset{O...H-O}{\diagdown}}}NO \rightleftarrows \left[ON{\overset{OH}{\underset{OH}{\diagdown}}}\right]^{\oplus} + NO_3^{\ominus}.$$
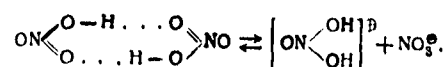
In support of this supposition they adduce a graph (Fig.75), in which the

curve of the change in the concentration of the " nitrocidium" ion coincides with

the curve of rate of formation of hexogen and various nitric acid concentrations.

Figure 75 illustrates the change in intensity of the infrared absorption band

at 1.017 micron at HNO_3 concentration in accordance with the determinations of

Dalmon and Freeman, who ascribed this band to associated molecules of acid.

Winkler (Bibl.57) comes to an analogous conclusion on the basis of an

investigation of the nitrolysis of urotropine in acetic acid.

Thexxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx

xxxxxxxx

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b)

Fig.74 - Effect of $HNO_3/C_6H_{12}N_4$ Ratio on Yield of Hexogen in Terms of Nitric Acid Consumed a) Hexogen yield with respect to HNO_3; b) Molar ratio $\dfrac{HNO_3}{C_6H_{12}N_4}$
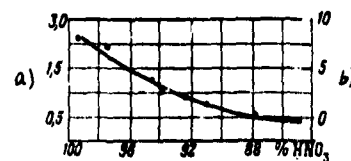
Fig.75 - Effect of Strength of Nitric Acid upon Concentration of "Nitrocidium " Ion and Initial Rate of Hexogen Formation. The hollow circles are the Dalmon and Freeman values taken as indices of the concentration of the "nitrocidium " ion. The solid circles are the initial rate of formation of hexogen at

$$\frac{HNO_3}{C_6H_{12}N_4} = \frac{40}{0} \text{ and } t = 0°.$$

a) Brightness of 1.017 micron absorption band;
b) Rate in $\dfrac{\%}{min}$

The urotropine nitrolysis reaction may be written in its general form

as follows:

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257 However, the small yield of hexogen and the large consumption of nitric

acid testify/the fact that this reaction is considerably more complex and is
    to

accompanied by side processes.

Hale and others (Bibl.58) hold that the hydrolysis of urotropine is such

a process. An investigation of the side products formed on the synthesis of

hexogen has demonstrated the presence of a certain amount of methylene dinitrate

XXXXXXX $CH_2(ONO_2)_2$ and trimethanolamine nitrate $N(CH_2ONO_2)_2$ in the concentrated

spent acid. On the basis XXXXXX thereof it is assumed that urotropine nitrolysis

proceeds in accordance with the following mechanisms:

$$CH_2$$

$+ 10HNO_3 \quad --$

$--- \quad + 3CH_2(ONO_2)_2 + NH_4NO_3 + 3H_2O;$

$+ 6HNO_3 \quad --$

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$$O_2N-N \overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{}} N-NO_2$$

$$\longrightarrow \quad CH_2 \qquad CH_2 \qquad + N(CH_2ONO_2)_3 + 3H_2O;$$

$$\underset{\displaystyle NO_2}{N}$$

$$\begin{array}{c} CH_2 \\ N \qquad\qquad N \\ CH_2 \qquad CH_2 \\ N \\ CH_2 \\ CH_2 \qquad\qquad CH_2 \\ N \end{array} \quad + 8HNO_3 \longrightarrow 2N(CH_2ONO_2)_3 + 2NH_4NO_3.$$

The intermediate products are comparatively stable in concentrated spent acid, but when allowed to settle or, particularly, upon dilution with water, they undergo saponification:

$$CH_2(ONO_2)_2 + H_2O \longrightarrow CH_2O + 2HNO_3;$$
$$N(CH_2ONO_2)_3 + 3H_2O \longrightarrow 3CH_2O + 2HNO_3 + NH_4NO_3.$$
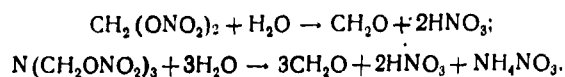
Formaldehyde is detected in dilute acid by its odor and may readily be driven off the neutralized solution with heating.

The most recent investigations do not confirm the mechanisms presented above. It was found that the side products IX differ in that composition, and the process itself goes stepwise.

Vroom and Winkler (Bibl.56), performing the nitrolysis of urotropine with 97% nitric acid at -40°, obtained a substance with a melting point of 98 - 99°,

upon   94%

which converted to hexogen ~~XX~~ subsequent treatment with/nitric acid. Analysis

showed that the substance is 3,5-dinitro-1,3,5-triazacyclohexone-1-nitrate (I):

$$O_2N-N \overset{CH_2}{\diagup \quad \diagdown} NH_2^{\oplus}NO_3^{\ominus}$$
$$CH_2 \quad CH_2$$
$$N$$
$$NO_2$$
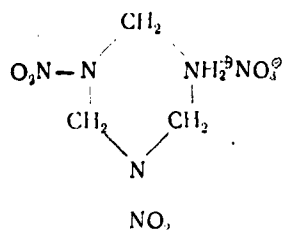
259   Conversion thereof into hexogen also was performed by treatment of suspension

I in nitromethane with boron fluoride or by treatment with P_2O_5 solution in

88% HNO_3.

3,5-Dinitro-1,3,5-triazacyclohexane-1-nitrate approximately equals hexogen ~~XXX~~ as

explosive properties, and its shock sensitivity is somewhat higher than for hexogen.

The authors hold that 3,5-dinitro-1-,3-5-triazacyclohexane-1-nitrate is an

                                by
intermediate in the nitrolysis of utropine/nitric acid, and that the final conversion

                                                        speed,
thereof into hexogen ~~XX~~ characterizes the overall process ~~████~~. This conversion is

inhibited by the side products of reaction and may lead to complete decomposition of

the intermediate product, resulting in a low hexogen ~~XXX~~ yield. The urotropine

nitrolysis reaction mechanism is, according to these investigations, the following:

$$\xrightarrow{\text{HONO}_2} \qquad \xrightarrow{\text{HONO}_2}$$

$$O_2N-N \qquad N--CH_2-N\begin{array}{c}CH_2OH\\CH_2OH\end{array} \xrightarrow[-N(CH_2OH)_3]{+H_2NO_3^{\ominus}}$$

$$O_2N-N \qquad NH^{\oplus}\cdot HNO_3^{\ominus} \xrightarrow{-H_2O} O_2N-N \qquad N-NO_2$$
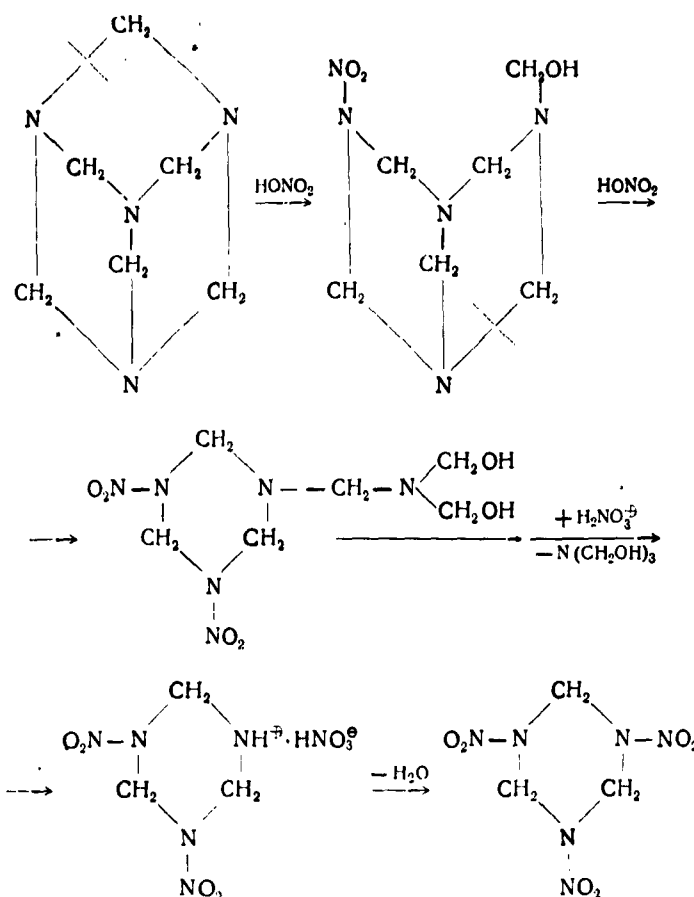
Berman and others (Bibl.59) do not believe the intermediate product in

hexogen process to be 3,5-dinitro-1, 3,5triazachlorohexane-1-nitrate. According

to their data, formation thereof occurs ⅪⅪⅪX when the reaction mixture is diluted

. 1-dimethylolaminomethyl-1,3,
as a consequence of the decomposition of ⅩⅪⅪⅪⅩⅩⅪⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩ

5-dinitro-1, ⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩⅩ 3,5-triazacyclohexane, the formula of which is

O$_2$N—N / N—CH$_2$—N with CH$_2$OH, CH$_2$OH groups; CH$_2$ bridges; N—NO$_3$
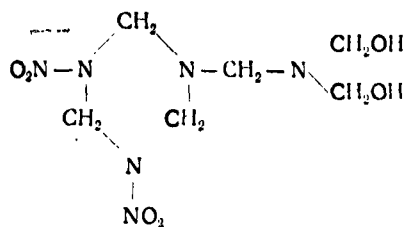
The composition of the latter in concentrated acid results in cleavage

of the dimethylamine group with conversion thereof into dimethylol nitroamide,

and the hexagonal ring yields 1-methylol-3,5-dinitro-1,3,5-triazacyclohexane.

This last compound converts to hexogen, but may also yield 3,5-dinitro-1,3,5-

triazacyclohexane-1-nitrate.

The process diagram looks like a series of nitration reactions of the

ternary amine

[process diagram with chemical structures]

$$\xrightarrow{\quad} \quad \xrightarrow[\text{conc.}]{HNO_3} \quad$$

minus HOCH$_2$—N—CH$_2$OH / NO$_2$

minus CH$_2$O v NH$_3$ plus dilute HNO$_3$
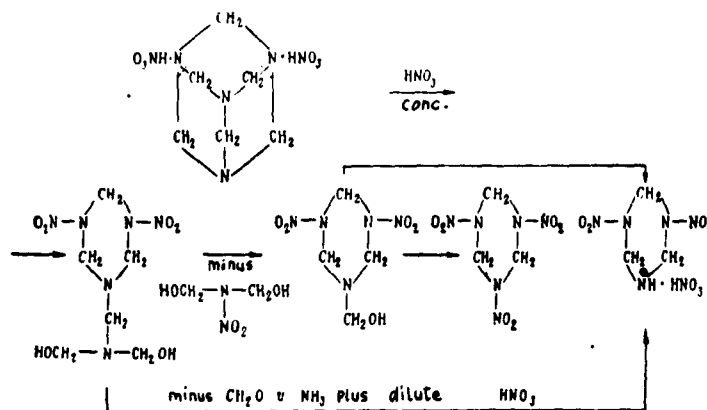
IXE 1-Dimethylolaminomethyl-3,5-dinitro-1, 3,5-triazacyclohexane yields

an insignificant amount, upon decomposition, of the linear compound 1,9-dihydroxy-2,

4,6,8-tetranitro-2,4,6,8-tetrazanonane (dihydroxypentamethylenetetranitroamine):

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$$HOCH_2-N-CH_2-N-CH_2-N-CH_2-N-CH_2OH$$

with NO_2 on each nitrogen
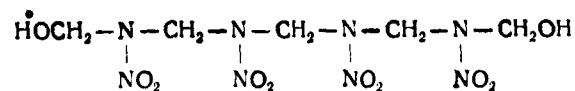
or, to be more exact, its nitrate ester.

Chute and associates (Bibl.55) have shown that when urotropine reacts with concentrated nitric acid, the consequence is not only hexogen but ~~dinitro~~ dinitropentamethylenetetramine (melting point 198°). Product yield rises with reduction in reaction time and increase in excess of HNO_3. The yields of dinitropentamethylenetetramine and hexogen/apparently mutually related. The

are

authors assume that this is due to a single common initial compound which may possibly be utropine dinitrate, the primary formation of which in the reaction, whereby urotropine is nitrolysed to hexogen, has been ~~demonstrated~~ demonstrated on the basis of comparison of the heats of nitrolysis of both products (Bibl.53,54).

261   According to Cerrione (Bibl.46), the formation of dinitropentamethylenetetramine is the first side reaction in the nitrolysis of urotropine by concentrated nitric acid:

$$\text{(urotropine)} + 2HNO_3 \rightarrow \text{(dinitropentamethylenetetramine)} + CH_2O + H_2O.$$

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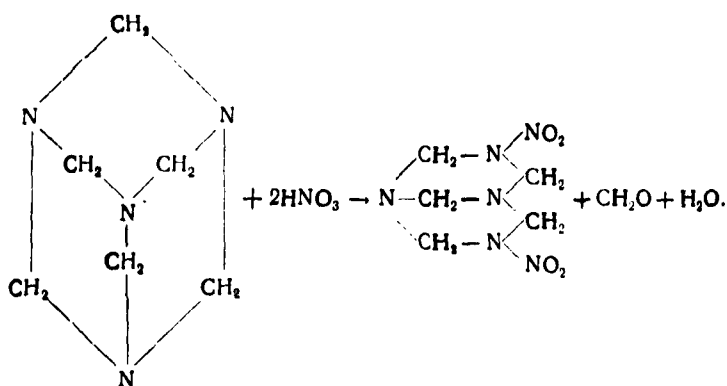
In a nitric acid solution, dinitropentamethylenetetramine behaves as a
di-acid base and is converted, to begin with, to the primary nitroamine:

$$N-CH_2-N\underset{\underset{CH_2}{\overset{CH_2}{\big|}}}{\overset{\underset{CH_3-N\diagup^{NO_2}}{}}{\diagdown}}_{CH_4-N\diagdown_{NO_2}} + 2H_2O \rightleftarrows N-CH_2 \cdot NH_2 \begin{matrix} CH_2 \cdot NH \cdot NO_2 \\ | \\ CH_3 \cdot NH \cdot NO_3 \end{matrix} + 2CH_2O,$$
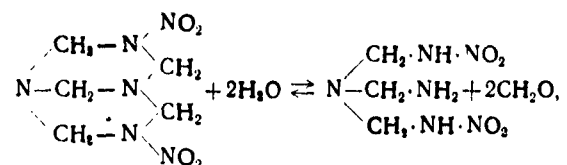
which then converts to dinitrotriaminotrimethylamine. Under given conditions
of nitrolysis, this latter converts partially into trinitrotriaminotrimethylamine:

$$N\begin{matrix} CH_2 \cdot NHNO_2 \\ -CH_2 \cdot NH_2 \\ CH_3 \cdot NHNO_2 \end{matrix} + HNO_3 \rightarrow N\begin{matrix} CH_3 - NH \cdot NO_2 \\ -CH_2 - NH \cdot NO_2 \\ CH_2 - NH \cdot NO_2 \end{matrix} + H_2O.$$
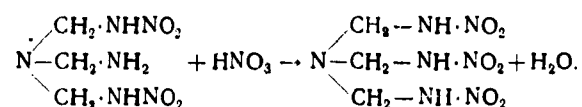
This substance is relatively stable in the cold, but at 60° it decomposes to
yield formaldehyde and ammonia.

Simultaneous with the formation of dinitropentamethylenetetramine and
its conversion products, urotropine nitrolysis is accompanied by the formation
of trinitrodiaminodimethylamine (TDA) in accordance with the following reaction:

$$3C_6H_{12}N_4 + 12HNO_3 \rightarrow 4O_2N \cdot N\begin{matrix} CH_2NHNO_2 \\ CH_2NHNO_2 \end{matrix} + 2H_2O + 10CH_2O.$$
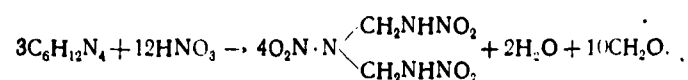
As distinct from the preceding one, this product does not dissolve in water.
Therefore, when hexogen is separated from the nitro mass by dilution with water,
trinitrodiaminodimethylamine is also liberated. This is an impurity in unstabilized
hexogen. In some cases, this substance constitutes 10% of the whole.

Trinitrodiaminodimethylamine slowly goes into solution at low temperature,

converting into soluble primary nitroamide - methylenedinitroamine:

$$O_2N \cdot N \Big\langle \begin{matrix} CH_2NHNO_2 \\ CH_2NHNO_2 \end{matrix} \quad \cdot \quad CH_2 \Big\langle \begin{matrix} NHNO_2 \\ NHNO_2 \end{matrix} + CH_2O + N_2O.$$
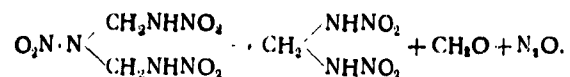
$((75 - 80^{\circ}))$

At ~~an~~ elevated ~~temperatures~~ temperature, this process proceeds with more complete

decomposition in accordance with the reaction:

$$C_2H_6N_6O_6 \longrightarrow 2CH_2O + 3N_2O + H_2O.$$
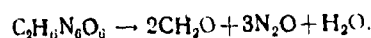
Therefore, what is termed the stabilization of hexogen is merely destruction of

trinitrodiaminodimethylamine.

A third side product of urotropine nitrolysis is methylene nitroamine

(or nitroiminomethane) $CH_2 = N \cdot NO_2$ (monomer of hexogen), which forms in

accordance with the reaction

$$C_6H_{12}N_4 + 4HNO_3 \longrightarrow 4CH_2 = N \cdot NO_2 + 2CH_2O + 2H_2O.$$
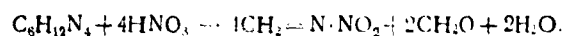
and
This compound exists only in solution ~~which~~ readily decomposes in accordance

with ^(the) equation

$$CH_2 \quad N \cdot NO_2 \longrightarrow CH_2O + N_2O.$$
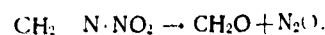
Cerrione regards hexogen as a trimer of methylene nitroamine, the greater

chemical stability of which he ascribes to its cyclic structure.

Cerrione indicates the following conditions of formation of hexogen and

the products accompanying it.

Hexogen is formed primarily at a 1:8 - 1:30 ratio urotropine to nitric acid

(or a modulus of 8 - 30), acid concentration in access of 95%, and nitrolysis

temperature over 10°. The product does not result if the modulus is less than 4

or more than 500, and if the concentration of nitric acid is less than ~~XXXX~~ 85%.

~~XXXXXXX~~ Trinitrodiaminodimethylamine forms primarily at a modulus of 8 – 20, a nitric acid concentration of more than 97%, and a temperature in ~~XXXX~~ excess of 10°, with a maximum yield of about 10%. The product is not obtained at a modulus of less than 4 or more than 500 and a concentration of acid less than 95%.

Dinitropentamethylaminetetramine is formed in more dilute ~~XXXXXX~~ acids. Maximum yield is achieved ~~XX~~ with 85% acid and a modulus of less than 10 (at a modulus of 3.5, the yield is 65%). The yield rises with reduction ~~XX~~ in the temperature of nitrolysis. Methylene nitroamine does not form if the concentration of nitric acid is less than 95% or if the modulus is less than 10. With rise in

is
modulus to 300, more methylene ~~XXX~~ nitroamine is ·formed than ~~XX~~ hexogen, and at

yield
a modulus of 700 – 800, the ~~XXXXX~~ thereof attains 70% in terms of methylene groups. With rise in temperature, the product yield increases.

Thus, the yield of trinitrodiaminodimethylamine is determined, in practice, by the same parameters as the ~~XXX~~ yield of hexogen. However, the maximum yield of this product is not great (10%). The conditions serving as an obstacle to the formation of dinitropentamethyleneteuramine and increasing the yield of hexogen (concentrated acid at high modulus) are most favorable to the formation of methylene nitroamine, and ~~XXXXXXXXXX~~ vice versa. The maximum yield of hexogen is obtained under conditions in which the curves of evolution of yield of dinitropentamethylenetetramine and increase in y̌ield of methylene nitroamine intersect. Simultaneous formation of dinitropentamethylenetetramine, methylene nitroamine, and hexogen, is a simple and convincing explanation of the few yield

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of the latter, occurring upon nitrolysis of urotropine by XXX nitric acid.

When weak nitric acid acts upon urotropine, the consequence is either
hydrolysis (under the effects of 80 - 90% acid) or formation of a salt (acid
concentration less than 80%). In the former instance, methylenediamine,
triaminotrimethylamine, and diaminodimethylamine are formed (the maximum yield
of these compounds achieves 80%) and in the second case it is urotropine dinitrate
that is formed. At very low concentrations of HNO_3 (less than 15%), the yield
of dinitrate diminishes as a consequence of its solubility in water.

Hexogen formed upon nitrolysis of urotropine will be almost entirely
dissolved in the spent acid. To separate it out, the solution XXX obtained has

263   to be diluted to an HNO_3 concentration of not more than 60%, at which the
solubility of hexogen is quite negligible. Dilution with water may be performed
in two ways: either by pouring the solution obtained into the necessary amount
of water or by adding water to the hexogen solution.

When the first method is employed, hexogen is XXXXXXXXXX separated out in
the form of very fine crystals. This greatly complicates XXXXX work therewith

further

(it is difficult to filter it, and filters clog). However, when the second method
is used, the spent acid is diluted with the water gradually, and hexogen formation
XX takes place less rapidly, XX making for the formation of larger crystals thereof.

This method is complicates somewhat by the circumstance that the spent XX acid
XXXX contains, not only hexogen, but side products of the synthesis which decompose
when diluted with water, as indicated above, to formaldehyde. Formaldehyde is
vigorously oxidized by nitric acid at concentrations of 60 - 65% or more, and the

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heat of reaction thus liberated is capable of heating the XXXXXX nitro mass

(inducing the composition of the hexogen). Therefore, the dilution must be

accompanied by careful adherence to the appropriate conditions of temperature.

In practice, this process is carried out in continuous apparatus (Bibl.45, 60),

and as a consequence the hexogen solution is poured, simultaneous with the water

diluting it, into an apparatus filled with dilute acid. The 50 - 60% spent acid

obtained as the result of dilution is not stable, as it contains formaldehyde,

which oxidizes readily XXX under these conditions. In order to increase the

stability of the spent acid, it is heated to 60 - 65°, at which temperature

formaldehyde is completely oxidized to CO_2. In industry, stabilization of the

spent acid by heating is performed simultaneous with dilution with water (Bibl.61).

Willson (Bibl.62) has XXXXXX patented a method of producing large hexogen

crystals which flow well. The method consists of adding to the nitration mixture

(produced by introducing urotropine into concentrated nitric acid) with agitation

and at a temperature of 65 - 70°, weak (50 - 70%) nitric acid containing a little

sodium nitrite. When the temperature, regulated by XXXXXXXXX external cooling,

rises, the side products begin to decompose. The gaseous products of the

containing
composition, XXXXXXX a large quantity of nitrogen oxides, are removed through the

system of ventilation and trapped in absorption equipment.

Destruction of the side product of the reaction, formaldehyde, by XXXXXX

oxidation thereof with nitric acid is one of the weakest sides of this method.

In actuality, the yield of hexogen from urotropine, computed on the formaldehyde

(from which urotropine is produced) is only 35 - 40%. The rest is oxidized, and

unproductive
this is the cause of a large XXXXXXXXX consumption of nitric acid.

500

This shortcoming is eliminated to some degree by the two-stage method

of producing hexogen from urotropine or from formaldehyde (Bibl.63). In the

first stage, urotropine is obtained by saturation of formalin (30% formaldehyde

solution) with gaseous ammonia:

$$6CH_2O + 4NH_3 \rightleftarrows C_6H_{12}N_4 + 6H_2O.$$
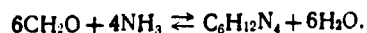
Under these conditions, urotropine is produced in the form of a 20 - 25%

solution. When weak nitric acid is added to the urotropine solution, the acid

comes down out of solution, almost quantitatively, in the form of urotropine

dinitrate:

$$C_6H_{12}N_4 + 2HNO_3 \rightarrow C_6H_{12}N_4 \cdot 2HNO_3.$$
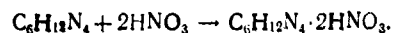
Thus, the evaporation operation is replaced by the operation of precipitation,

which is cheaper and more productive. II It proved possible, on the same principle,

to recover the formaldehyde from the spent acid. After washing and drying, the

pressed crystals of urotropine dinitrate convert into hexogen for which only five

264   parts concentrated nitric acid are employed, by weight.

The hexogen yield from the dinitrate is approximately 5% larger than from

urotropine. Moreover, the hexogen yield may be increased at the expense of the

formaldehyde in the dilute spent acid. With this purpose, the spent acid is diluted

at low temperature ($15 - 20^{\circ}$), and then the acid is neutralized by ammonia to

protect the formaldehyde from oxidation. The result is the formation of urotropine

and ammonium nitrate:

$$6CH_2O + 4NH_3 \rightleftarrows C_6H_{12}N_4 + 6H_2O;$$
$$HNO_3 + NH_3 \rightarrow NH_4NO_3.$$
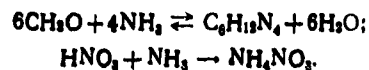
The urotropine is precipitated as urotropine dinitrate by weak nitric

acid. The filtered spent acid is a 50% solution of ammonium nitrate and goes

to evaporation.

In Germany, during World War II, various other methods (Bibl.47) were

employed in addition to the major method of nitrolysis.

When hexogen was produced by the "W" method (suggested in 1934 by Wolfram),

the raw material is formaldehyde which is converted, by a series of successive

into
reactions, ~~XXXXXXX~~ potassium cyclotrimethylenetriimino sulfate, ~~XXXXX~~ termed

"white salt", and is then nitrated ~~XXX~~ to hexogen. The following reactions

occur herein:

Sulfaminic
1) ~~XXXXXXX~~ acids is formed by the action of ammonia on sulfur anhydride:

$$SO_3 + NH_3 \rightarrow HSO_3NH_2;$$
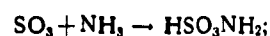
sulfaminic
2) Reaction of ~~XXXXXXX~~ acid with potassium carbonate results in the

formation ~~XX~~ of potassium sulfaminate:

$$2HSO_3NH_2 + K_2CO_3 \rightarrow KSO_3NH_2 + H_2O + CO_2;$$
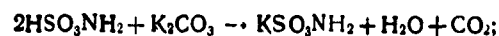
3) Further, condensation of the potassium sulfaminate ~~XX~~ with formaldehyde

occurs to form "white salt":

$$3KSO_3NH_2 + 3CH_2O \rightarrow \begin{array}{c} CH_2 \\ KO_3S-N \quad\quad N-SO_3K \\ CH_2 \quad CH_2 \\ N \\ SO_3K \end{array} + 3H_2O;$$
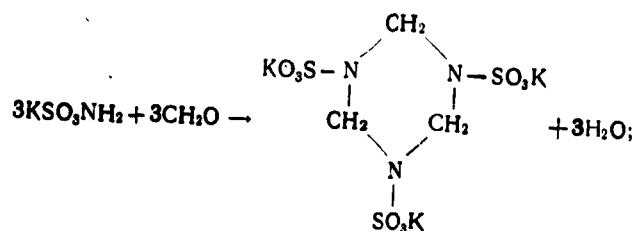
4) The action of concentrated mixed acid upon "white salt" results in

hexogen:

$$KSO_3-N \overset{CH_2}{\underset{CH_2 \quad CH_2}{\overset{\big|}{\underset{N}{\big|}}}} N-SO_3K \quad +3HNO_3 \rightarrow$$
$$\underset{SO_3K}{}$$

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$$\rightarrow \quad O_2N-N \overset{CH_2}{\underset{CH_2 \quad CH_2}{\big|}} N-NO_2 \quad +3KHSO_4.$$
$$\underset{NO_2}{N}$$
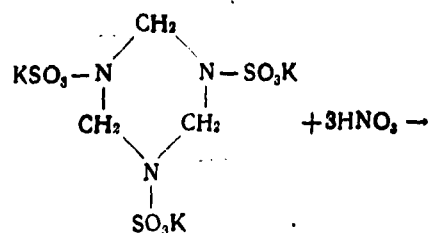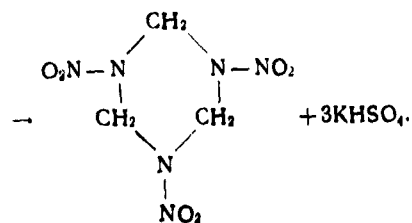
The hexogen yield is approximately 80%, in terms of the formaldehyde

consumed.

The "E" method (its inventor was Elbe) is based on condensation of

paraformaldehyde with ammonium nitrate to hexogen:

$$(CH_2O)_3 + 3NH_4NO_3 \rightarrow \quad O_2N-N \overset{CH_2}{\underset{CH_2 \quad CH_2}{\big|}} N-NO_2 \quad +6H_2O.$$
$$\underset{NO_2}{N}$$
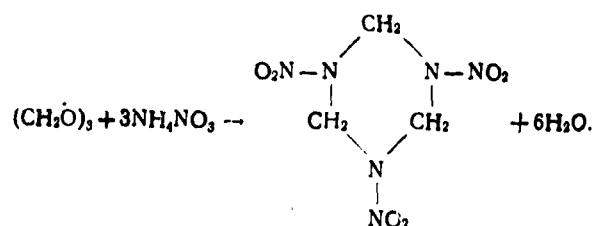
The reaction is performed in an acetic anhydride medium, in which pulverized

paraformaldehyde and dry ammonium nitrate are introduced, with energetic agitation.

The acetic anhydride takes up water, converting it to acetic acid.

The reaction goes better if boron fluoride is employed. This is

simultaneously a dehydrator and <s>presenter</s> catalyst. The acetic anhydride is first

saturated with boron fluoride, to form the compound $(CH_3CO)_2OBF_3$ (Bibl.64).

However, this method results in hexogen having a low melting point, because

it contains a large quantity (up to 20%) of impurities.

Hexamethylenetetramine dinitrate (Bibl.65) has been isolated

from the reaction products of paraformaldehyde and ammonium nitrate in glacial

acetic acid. The authors hold this to be an intermediate product in the

formation of hexogen under these conditions.

The "K" method (due to Knoffler) consists of treating a mixture of urotropine

and ammonium nitrate with concentrated sulfuric acid. Formation of the hexogen

apparently proceeds in accordance with two reactions:

$$1) \ C_6H_{12}N_4 + 4HNO_3 \rightarrow C_3H_6(NNO_2)_3 + 3CH_2O + NH_4NO_3;$$
$$2) \ 3CH_2O + 3NH_4NO_3 \rightarrow C_3H_6(NNO_2)_3 + 6H_2O,$$

or, in sum:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 \rightarrow 2C_3H_6(NNO_2)_3 + 6H_2O.$$
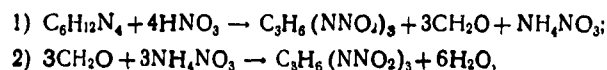
The yield of hexogen with respect to formaldehyde is 60%. A shortcoming

of this method is the large consumption of nitric acid and ammonium nitrate that

has to be metered in. This is because ammonium nitrate is not very good as a

condensation medium.

When acetic anhydride is employed as the dehydrator, the conditions for

condensation of formaldehyde and ammonium nitrate improve. Simultaneously, more

complete conversion of HNO_3 to $NO_2^{\oplus}$, which is an active nitrating agent (Bibl.66),

takes place. This method is called the "KA" method, as distinct from the preceding

one. There are two versions of this method.

In accordance with the first version, ammonium nitrate is suspended in acetic anhydride, and nitric acid and uretropine are added simultaneously to the suspension. An increase in yield is achieved by employing the dinitrate of urotropine for nitration, instead of urotropine itself.

The reaction goes in accordance with equation

$$C_6H_{12}N_4 \cdot 2HNO_3 + 2NH_4NO_3 + 2HNO_3 + 6(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2C_3H_6(NN\dot{O}_2)_3 + 12CH_3COOH + 118 \ \text{Kcal/mole}$$
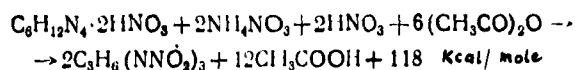
As a consequence of the insignificant solubility of hexogen in acetic acid at 20°, the reaction mass is not diluted with water.

During World War II, hexogen was produced in the United States, Canada, and England, by Bachman-Ross methods, analogous to the German "KA" method. Nitrolysis of urotropine by nitric acid was performed in the presence of ammonium nitrate, acetic acid, and acetic anhydride. The technological procedure employed in the Bachman process differs somewhat from the "KA" method (Bibl.67, 68, 69, 70). According to Ross (Bibl.70) the formation of hexogen from urotropine occurs as follows:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2C_3H_6(NNO_2)_3 + 12CH_3COOH;$$
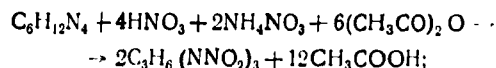
in which 140 kcal/mole of heat is liberated (the energy of activation is 12 kcal).

The reaction occurs in a number of stages and is accompanied by the formation of side products which are capable, under given circumstances, of becoming the major products. The intermediate reaction product is apparently

urotropine mononitrate (Bibl.53, 71).

Urotropine goes into reaction almost instantaneously (within 5 sec at 35°) one molecule of hexogen being formed as a result. Addition of NH_4NO_3 results in the formation of a second molecule of hexogen (Bibl.72,73). This shows that the second molecule of hexogen is formed from the cleavage products of urotropine and ammonium nitrate.

Hexogen produced by the Bachman–Ross method contains up to 10% oxygen (tetranitrotetrazacyclooctane) (Bibl.74).

With the object of studying the mechanism of the reactions occurring, ammonium nitrate containing a~~one~~ labeled nitrogen atom (N^{15}) in the ammoni~~a~~um group ($N^{15}H_4NO_3$) was employed. It was found that hexamethylenetetramine is subjected to two major types of decomposition, resulting in the formation of compounds containing three atoms of amine nitrogen ~~XXXXXXXX~~ (hexogen) and a compound containing four atoms of amine nitrogen ~~XXXXXXXX~~ (oxygen). If the medium is highly acid, and the nitrating agent is highly active, the consequence is cleavage of the former type, resulting in the formation of hexogen. If acidity is low, and activity of the nitrating agent is also, cleavage of the second type resulting in the production of oxygen occurs.

Thus, the hexogen-producing reaction is intimately related ~~XXXX~~ to the ~~XXXXXX~~ oxygen-producing reaction.

Epstein and Winkler (Bibl.75) determined the relationship of the hexogen and oxygen yield to the amount of NH_4NO_3 (Fig.76) introduced into the reaction. These authors hold that urotropine converts at least to two intermediate compounds, one

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of these capable of serving as a source of hexogen and oxygen, while the

other will yield hexogen only. Thus, if the NH_4NO_3 is added later, the hexogen

yield is not more than 30%, while postponement of the introduction of NH_4NO_3 is

not reflected in the oxygen yield.

The optimum yield of hexogen (70% $C_6H_{12}N_4 \rightarrow 2C_3H_6(NNO_2)_3$) occurs at a

molar ratio of $C_6H_{12}N_4$: HNO_3 : $(CH_3CO)_2O$ 1:5.2 : 20 and 2.7 moles NH_4NO_3. Further

increase in the amount of NH_4NO_3 has no practical effect upon the hexogen yield.

267   The optimum yield (25% $C_6H_{12}N_4 \rightarrow 1$. $C_4H_8(NNO_2)_4$) at the same ratios of $C_6H_{12}N_4$,

HNO_3 and $(CH_3CO)_2O$ occurs in the presence of XX 2.3 moles XXXXXX NH_4NO_3.

The amount of nitric acid has a significant influence upon the yield of

hexogen and oxygen. At a $C_6H_{12}N_4$:$(CH_3CO)_2O$:NH_4NO_3 = 1 : 20 : 3 ratio, the optimum

yield of both products is obtained in the presence of 6 moles HNO_3 (Fig.77).

Simultaneous increase in the amount of NH_4NO_3 shifts the optimum yield of hexogen

and oxygen toward higher values (see Fig.76).

With increase in the amount of $(CH_3CO)_2O$, the yield of hexogen rises, and

with the ratio $C_6H_{12}N_4$: HNO_3 : NH_4NO_3 = 1 : 5.2 : 3 achieves a maximum at

                    Further
15 - 20 moles of $(CH_3CO)_2O$. XXX increase in the amount of $(CH_3CO)_2O$ does not

lead to an increase in the hexogen yield. The yield of oxygen is at a maximum at

15 moles of $(CH_3CO)_2O$ (see Fig.77).

Investigations serve as the basis for suggesting the following mechanism

of urotropine nitrolysis by nitric acid in the presence of ammonium nitrate and

acetic anhydride (Fig.78) (Bibl.75). Stages 5, 6, and 7 regulate the process rate

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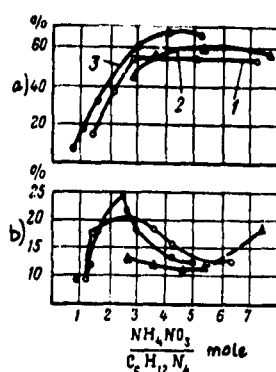
Fig.76 – Effect of Quantity of NH_4NO_3

upon Yield of Hexogen and Oxygen

Curve	Molar Ratios			
No.	CH.COOH	HNO,	(CH.CO),O	C.H.N.
1	194	5,2	20	1
2	194	9,5	20	1
3	104	5,2	20	1

a) Hexogen yield; b) Oxygen yield
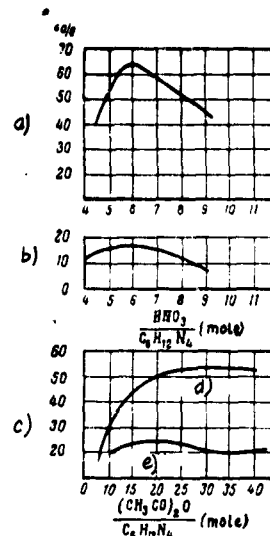
Fig.77 – Effect of Amount of HNO_3

and $(CH_3CO)_2O$ upon Yield of Hexogen

and Oxygen

a) Hexogen yield; b) Oxygen yield;

c) Yield of Hexogen and oxygen;

d) Hexogen; e) Oxygen

in the production of hexogen under the Bachman-Ross reaction. If stage 5 is

eliminated by slowing the ammonium nitrate addition reaction, the consequence

is the formation of linear products, but there is no reduction in nitric acid

consumption, inasmuch as, instead of hexogen, formation of diacetoxytetramethylene-

dinitroamine occurs (Bibl.1), containing the same number of nitro groups:

$$CH_3-C-O-CH_2-N-CH_2-N-CH_2-N-CH_2-O-C-CH_3.$$
$$\;\;\;\;\; \underset{O}{\|} \quad\quad \underset{NO_2}{|} \quad \underset{NO_2}{|} \quad \underset{NO_2}{|} \quad\quad \underset{O}{\|}$$
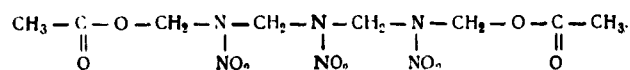
Replacement of acetic anhydride by nitric acid anhydride (at a ratio of

$C_6H_{12}N_4$: HNO_3 : N_2O_5 = 1 : 11.7 : 3.9) leads to the ~~XXXXX~~ formation of

. dinitrooxytetramethylenetrinitroamine (Bibl.55) in addition to the hexogen

$$O_2NOCH_2 - N - CH_2 - N - CH_2 - N - CH_2ONO_2.$$
$$\underset{NO_2}{|} \quad \underset{NO_2}{|} \quad \underset{NO_2}{|}$$
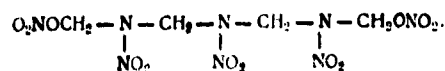
268   Chute and others (Bibl.55) produced dinitropentamethylenetetramine by

treating urotropine dinitrate with acetic anhydride for 4 days. Nitrolysis by

the latter by a mixture of 99.6% nitric acid and NH_4NO_3 (in a molar ratio of

1.78 : 1) at 25° and $70 - 75^o$ led to the formation of a mixture of 52% hexogen

and 17% oxygen. Change in the ratio between HNO_3 and NH_4NO_3 to 1 : 1 increases

the yield of hexogen to 57%, and the yield of oxygen is diminished accordingly

(Bibl.76):
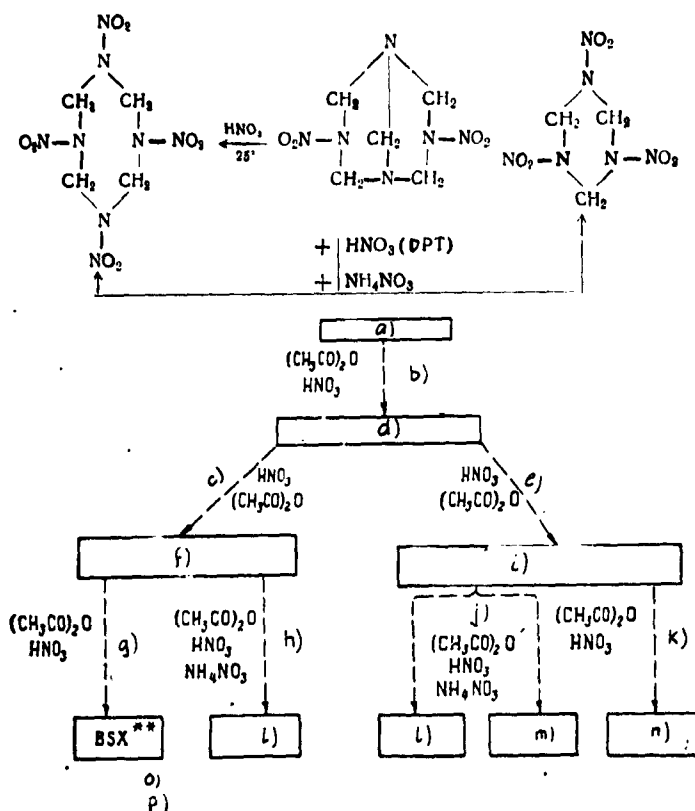
or
Fig.78 - Nitrolysis ~~XXXXXXXXXXXXXXX~~ Urotropine by Nitric Acid
in the Presence of Ammonium Nitrate and Acetic Anhydride

(For captions, see next page)

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Fig.78 (cont'd)

a) Urotropine; b) Stage 1 (very fast); c) Stage 2 (fast); d) By atomic

compound; e) Stage 3 (fast); XIXXIXXXXXXXXXXXXXXXXXXXXXX f) Six-term-ring

compound; g) Stage 4 (slow); h) Stage 5 (slow); i) Carbon compound for

oxygen and hexogen (possibly DPT*); j) Stage 6 (slow); k) Stage 7 (slow);

l) Hexogen; m) Oxygen; n) Linear products; o) Dinitropentamethylenetetramine;

XXXXXXXXXXXX p) Diacetoxytetramethylenetrinitroamine

When dinitropentamethylenetetramine is treated with nitric acid containing

N_2O_5 at 0 – 25°, a linear compound 1,9-dinitrooxy-2,4,6,8-tetranitro-2,4,6,8-

tetrazanonane (III):is isolated:

$$NO_2 - OCH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2O - NO_2, \qquad (III)$$
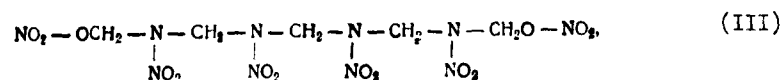
which, under the influence of sodium acetate solution in acetic acid is converted

to 1,9-diacetoxy-2,4,6-tetranitro-2,4,6,8-tetrazanonane:

$$CH_3 - \underset{\underset{O}{\|}}{C} - OCH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2 - \underset{\underset{NO_2}{|}}{N} - CH_2O - \underset{\underset{O}{\|}}{C} - CH_3, \qquad (II)$$
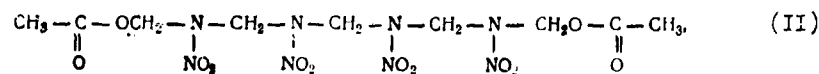
obtained earlier by Bennett and others (Bibl.77).

269   1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane may be obtained

directly from dinitropentamethylenetetramine by treating XX it with a mixture of

to this system
HNO_3 and $(CH_3CO)_2O$ at 44°. Addition of NH_4NO_3/at 65 – 70° directs the reaction

towards the formation of hexogen (Bibl.74).

Marcus and Winkler (Bibl.78) also obtained XXXXXXXX diacetoxy-2,4,6,8-tetranitro-

XXXXXXXXXXXX 2,4,6,8-tetrazanonane from dinitropentamethylenetetramine through the

following intermediate: 2-acetoxymethyl-4,6,8 trinitrocyclotetramethylenetetramine

(PHX):

$$NO_2$$
$$|$$
$$N$$
$$CH_2 \quad CH_2$$
$$O_2N-N \qquad N-NO_2$$
$$CH_2 \quad CH_2$$
$$N$$
$$CH_2OOCH_3$$
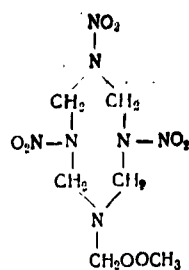
The mechanism due to McKay and others (Bibl.76) appears as follows:

II

$$\rightarrow CH_3-C-O-CH_2-N-CH_2-N-CH_2-N-CH_2-N-CH_2-O-C-CH_3$$

with O (double bond) at the ends, NO_2 groups on the N atoms, and a fused ring system:

$$NO_2$$
$$N$$
$$CH_2 \quad CH_2$$
$$O_2N-N \qquad N-NO_2$$
$$CH_2 \quad CH_2$$
$$N$$
$$CH_2OOCH_3$$

$$N$$
$$CH_2 \quad CH_2$$
$$O_2N-N \quad CH_2 \quad N-NO_2$$
$$CH_2 \quad CH_2$$
$$N$$

III

$$NO_2-OCH_2-N-CH_2-N-CH_2-N-CH_2-N-CH_2O-NO_2 \leftarrow$$

(with NO_2 groups on each N)

Left side: $CH_3COONa + CH_3COOH$

Middle arrow label: $HNO_3 + (CH_3CO)_2O$
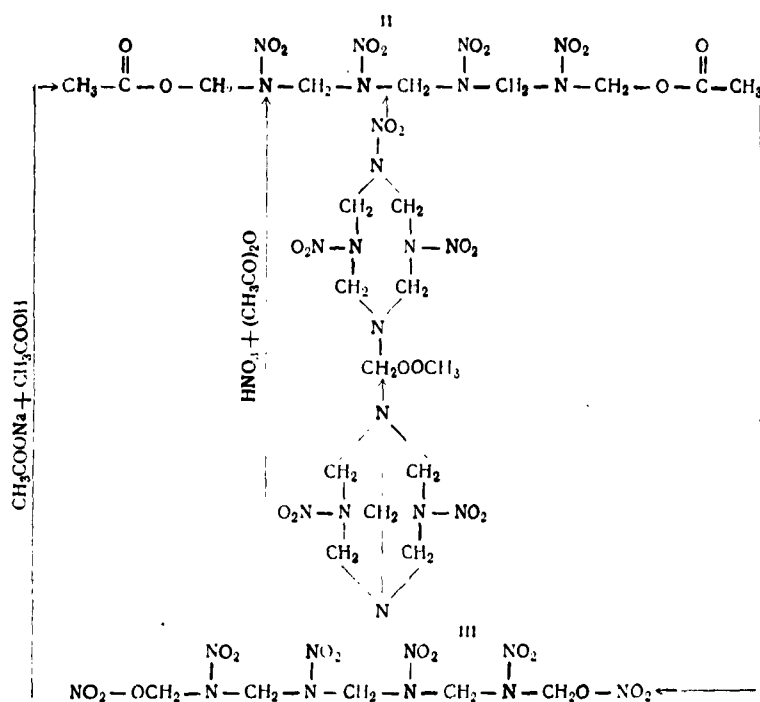
Formation of oxygen in the presence of ammonium nitrate in a solution consisting of the system $HNO_3 - (CH_3CO)_2O$ means that NH_4NO_3 either facilitates the removal of formaldehyde or prevents etherification. These effects are apparently interrelated. Thus, for example, it is known that when ammonium nitrate dissolves in this mixture, the reaction temperature has to be raised

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60 - 70°, before the nitric acid becomes effective for etherification, or for

nitrolysis. Raising of the temperature is apparently necessary in order to

clean off the formaldehyde.

270   Thus, the mechanisms of Chute (Bibl.55), McKay, Richmond, and Wright

(Bibl.77), ~~XXX~~ as supplemented by Marcus and Winkler (Bibl.78) support the right

side of the general mechanism due to Epstein and Winkler (Bibl.75).

The literature also describes a number of ~~XXXX~~ the methods of producing

hexogen, but these have hitherto not been practical applications.

Methods (Bibl.79, 80) have been suggested for the production of hexogen

that, it is claimed, yield 90% yields, based on treatment of ~~XXXXXXXXX~~ urotropine with

nitric acid in the presence of P_2O_5 according to one ~~XXXXXX~~ patent, and in the

presence of acetic anhydride, ammonium nitrate, and lithium nitrate in accordance

with a second patent.

One mole urotropine is added, in 25 min, at 65°, to a mixture of 4.25 moles

HNO_3, 4.16 moles NH_4NO_3, 5.7 moles$(CH_3CO)_2O$ and 2.58 moles $Li(NO_3)_2$.

Caesar and Goldfrank (Bibl.81) have proposed the production of hexogen by

nitration of utropine by a solution of N_2O_5 in chloroform, carbon tetrachloride,

or dichloropropylene. According to the authors, nitrolysis by this method may be

performed either batchwise, or continually, in either case the product yield is

high.

An interesting method of preparing chemically pure hexogen was developed

by Brockman and others (Bibl.82). The initial product is 1,3,5-trinitroso-

1,3,5-triazacyclohexene, which is made from urotropine. The nitroso compound

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reacts vigorously (with ignition) with concentrated XXX nitric acid at low

temperature. However, at a temperature of $-40°$, the reaction goes calmly. The

authors oxidized a mixture in 82 equivalents of 99% HNO_3, three equivalents of H_2O_2

and 3.7 equivalents XX of H_2O (in the resultant mixture, the HNO_3 concentration

is 92 - 94%). This solution was cooled to $-40°$, and one equivalent of nitroso

compound was added to it, gradually, with vigorous agitation. The nitroso compound

dissolved under these conditions. When the consequent solution was decanted

onto ice, a bright yellow precipitate came down, which was 1-nitroso-3,5-dinitro-1,

3,5-triazacyclohexene. When this product was returned to the same oxidizing

XXXX mixture at $-40°$, and the solution was allowed to heat up to $20°$, it converted

to chemically pure hexogen with a melting point of $204°$. The product yield was

about 75% of the theoretical. Thus, the reaction of conversion of 1,3,5-trinitroso-

XXXXXXXXXXXXXX 1,3,5-triazacyclohexene to hexogen proceeds as follows:
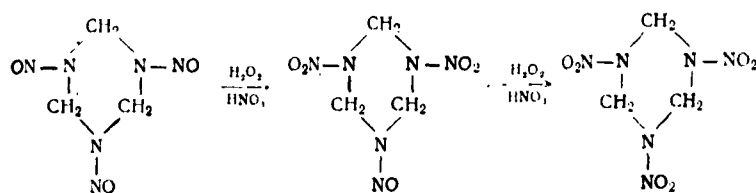
Properties of hexogen. Hexogen consists of white odorless and tasteless

crystals. As shown by the most recent investigations, it is a powerful poison

(Bibl.83), and therefore safety rules must be rigorously adhered to in working

with it.

The specific gravity of hexogen is 1.816, and its gravimetric density is

0.8 - 0.9 kg/ltr. Pressing at a pressure of 2000 kg/cm^2 yields a density of

1.73. The melting point is 204.5 - 205° (Bibl.82). The technical product obtained

by direct nitrolysis of urotropine by nitric acid fuses at 202°, XXXXXX

corresponding to approximately 1% impurities content. By boiling with nitric

may be
acid, the melting point of hexogen XX raised to 203.5°, and repeated

recrystallization out of acetic acid raises the melting point to 204.5 - 205°

(Bibl.82). The specific heat of hexogen at 0.30 kcal/gm°C, and the heat of

crystallization is 21.3 kcal/mole (Bibl.84).

Hexogen is non-hydroscopic, and poorly soluble in water, ether, alcohol,

XXXX chloroform, and weak nitric acid. It is readily soluble in acetone and

concentrated nitric acid. The solubility of hexogen in various solvents (Bibl.85,86)

is presented in Tables 81 and 82.

The solubility of hexogen in boiling butyl acetate is XX 7.8%.

271   Table 83 presents data on the solubility of hexogen in aniline and in

mononitrotoluene, and Table 84 presents the solubility in a number of XXX new

solvents (Bibl.87).

Table 81

a)	b)	c)
Water	15	0,01
"	100	0,15
Acetone	20	7,413
"	53	17,50
Ethyl alcohol	20	0,104
Methyl alcohol	21	0,187
Benzene	21	0,015
Toluene	18	0,032
	20	0,008
Chloroform	20	0,038
Anhydrous ether	18	d)
CS$_2$ and CCl$_4$	25	12,7
Cyclohexane	97	27,0
"	25	1,5
	97	12,4
Nitrobenzene		
"		

Table 2

a)	b)
93	12,5
80	2,2
70	0,44
60	traces

a) Solvent; b) Temperature, $^\circ$C; c) Solubility
of hexogen in 100 gm solvent, gm; d) Does not
dissolve

a) HNO$_3$ concentration, %;
b) Hexogen solubility, %

Table 83

a)	30	40	60	80	95	108	135	140	154
b)	0,40	—	2,55	3,65	4,20	—	4,74	—	5,12
c)	—	1,93	3,81	—	9,03	12,22	27,4	29,43	—

a) Temperature, $^\circ$C; b) Solubility in aniline in %; c) Solubility in
mononitrotoluene in %

Table 84

a)	b)						
	c)	d)	e)	f)	g)	h)	i)
25	1,6	2,8	2,6	3,1	1,5	1,6	31,9
100	9,3	13,3	10,0	13,5	7,9	6,4	71,1

a) Solubility of hexogen at temperature, $^\circ$C; b) Solvents; c) Cellosolve; d) Methyl-cellosolve;
e) Carbitol; f) Methyl-carbitol; g) Acetate-carbitol; h) Butyl-carbitol;
i) Dimethylformamide

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Annotation. Cellosolve – is ~~glycoldimethylether~~ glycol monoethyl ether $CH_2(OH)CH_2(OC_2H_5)$;

methyl-cellosolve – is ~~XXXYXXXXXXXXX~~ ethylene glycol methylether $CH_2(OH)CH_2(OCH_3)$;

carbitol – is diethylene glycol ethyl ether $CH_2(OH)CH_2-O-CH_2-CH_2(OC_2H_5)$;

Methyl-carbitol is diethyleneglycol methylether $CH_2(OH)CH_2-O-CH_2-CH_2-CH_2(OCH_3)$;

acetate–carbitol is diethyleneglycol monoacetate ~~XXXXXXXXXXXX~~ monomethylether

(CH_3COO) • $CH_2-CH_2-O-CH_2-CH_2(OCH_3)$; butyl-carbitol is diethyleneglycol butylether

(C_4H_9O) • $CH_2-CH_2-O-CH_2-CH_2(OH)$.

Hexogen is crystallized out of acetone in the ~~monocyclic~~ monoclinic system, and out

of nitric acid in the tetragonal system.

Table 85 illustrates the eutectic mixtures formed by hexogen and other

organic substances (Bibl.86).

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Ta: Table 85

a)	b)	c)
Para–nitrotoluene	about 0,5	50,4
Para–nitroanisole	about 0,5	50,9
α–nitronaphthalene	about 1,5	55,4
Meta–dinitrobenzene	8	85
α–trinitrotoluene	2,5	78,6
1,3,5–trinitrobenzene	about 3,3	113,8
Picric acid	12	112,9
Tetryl	10	118,1
Dimethyldiphenylurea	17	112,4
Diethyldiphenylurea	3	70,4
Camphor	22	137,5

a) Organic substance; b) Quantity of hexogen in the eutectic, %;

c) Freezing point of eutectic, °C

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Hexogen is stable to solar radiation.

Hexogen is a neutral substance that does not react with dilute acid. Concentrated sulfuric acid composes it in accordance with ɡᑫᑫᑫᑫᑫ equation (Bibl.88).

$$(CH_2NNO_2)_3 + 2H_2SO_4 \rightarrow 3CH_2O + 2HNSO_5 + 2N_2 + H_2O.$$

This reaction is explained by the insignificant yield of hexogen when urotropine is nitrated with mixed ᑫᑫᑫ sulfuric and nitric acid even containing a little H_2SO_4 (the mixed acid consists of: 88% HNO_3; 8% H_2SO_4; 4% H_2O).

Hexogen dissolves in concentrated nitric acid in the cold without decomposition and may be precipitated therefrom simply by diluting the acid with water.

When hexogen is treated with alkali dissolved in an aqueous acetone solution, hydrolysis occurs (Bibl.89). The energy of activation of this hydrolysis is equal to 14 kcal/mole (Bibl.90). The high speed of hydrolysis of hexogen by dilute caustic soda solution is employed in industry to remove hexogen from the apparatus (Bibl.60).

The hydrolytic cleavage of hexogen also occurs when it is cooked with
                an
water in/autoclave at a temperature over 150° (the technical method of removing acid from the hexogen crystals). HNO_3, CH_2O, NH_3 (as nitrate) as well as $C_6H_{12}N_4$ are found in the mother liquors (Bibl.91). The hydrolysis apparently goes in accordance with the following equation:

$$(CH_2NNO_2)_3 + 6H_2O \rightleftharpoons 3H_2CO + \frac{3NH_3 + 3HNO_3}{3NH_4NO_3}.$$
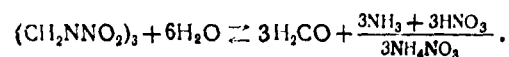
Hexogen, prepared by the acetic anhydride method contains ᑫᑫᑫᑫ oxygen as

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an impurity.

The amount of oxygen in the hexogen is determined by thermal analysis

based on the melting point of the hexogen-oxygen mixture (Fig.79).(Bibl.82).

The bottom line of this mechanism represents the first observed softening of

specimen,
XXXXXXXXX whereas the upper line denotes the disappearance of the final crystal

thereof.

273   Hexogen obtained by the method of nitrolysis contains bound HNO_3 and

oxyhexogen (up to 0.04%). Oxyhexogen

$$CH_2$$
$$O_2N-N \qquad N-NO_2$$
$$| \qquad |$$
$$CH_2 \qquad CH_2$$
$$O$$
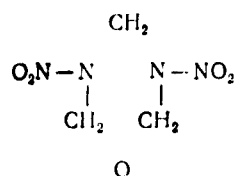
is a white crystalline substance with melting point of 92 - 98° and crystallizes

out of a mixture of water and acetone. Its solubility in acetone is greater than

that of hexogen, and therefore it remains in the mother liquor. Oxyhexogen is

stable in the pure form and therefore its presence in hexogen does not affect

the stability of the latter (Bibl.91).

Hexogen is highly stable and may be stored for months at 50° without

decomposition. It withstands XXXX the Abel test at 60° for more than 60 hrs.

The stability of chemically pure hexogen considerably exceeds that of tetryl,

but the stability of the technical product is not infrequently lower than this.

There may be two reasons for the inadequate stability of technical hexogen.

The first is the presence in the product of diacetoxytetramethylenetrinitroamine

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as an impurity (BSX). This latter may be present in hexogen obtained by the

acetic anhydride method. Hexogen is stabilized by long-term boiling in water,

Fig.79 - Diagram of Fusibility of

Hexogen-Oxygen Mixture

a) Oxygen; b) Hexogen

during which the unstable ~~XXXXXXXX~~

diacetoxytetramethylenetrinitroamine

decomposes.

A second reason for the inadequate

tecnnical hexogen
stability of ~~XXXXXXXXXX~~ is the presence

of nitric acid therein that has not been

washed out. This shortcoming is inherent

in hexogen obtained by the nitrolysis

method, in which the hexogen is isolated from 55% nitric acid. The hexogen crystals

formed contain bound nitric acid, the removal of which occurs very slowly even upon

long boiling and the presence of small crystals. In order to achieve 0.13% hexogen

acidity, a long period of washing (40 - 50 hours) is required. This is difficult to

achieve under industrial conditions (Bibl.91). The presence of a considerable

amount of nitric acid in the technical hexogen induces ~~XXXXX~~ corrosion and renders

utilization of standard specimens difficult in determining stability. It has

been shown (Bibl.91) that nitric acid virtually does not reduce the stability of

hexogen. Thus, a second ~~XXXX~~ reason for the low stability of ~~XXXXXXXXXX~~ technical

hexogen is essentially merely apparent.

The acid present in hexogen destroys the packaging material upon storage.

It has been suggested that this phenomenon be combated by adding 3 - 4%, N,

~~XXX~~ N'-diphenylethylenediamine or some other similar substance, capable of

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reacting with nitrogen oxide, to the packaging (Bibl.92).

    Upon heating, hexogen starts to decompose with noticeable rapidity to

200°. The flash point is 230° (Bibl.93). In the open air, hexogen burns with

a bright white flame, leaving no residue, whereas upon rapid heating it decomposes

with explosion.

    Pure hexogen is thermally stable.

    The comparative data on stability due to Hansen (in terms of pH) after

heating 5 gms of XXXXXXXX/substance^a at 132° are presented in Table 86.

274   Data on the stability of mixtures containing hexogen, ammonium nitrate, and

di cyanodiamide, are presented in a work by Brandimarte (Bibl.94).

Table 86

a)	b)	c)	d)
0	6,53	6,85	6,56
1	—	3,11	3,03
2	5,81	2,96	2,64
3	—	—	2,32
4	—	2,89	2,22
5	5,73	—	red fumes
6	—	—	—
7	—	2,73	—
8	5,68	2,68	—

a) Heating time, hrs; b) Hexogen; c) Tetryl; XXXXX d) PETN

    In stop sensitivity, hexogen occupies a position midway between tetryl

and PXXX PETN. In impact testing, a 2 kg weight causes explosion of hexogen

when dropped from a height of 30 - 32 cm. Sensitivity in the standard test

(p = XXXXXX 10 kg, h = 25 cm) XXXXXX is 80%.

explosive
The heat of ~~explosive~~ decomposition of hexogen is 1320 kcal/kg, the

explosion   velocity
volume of gaseous ~~explosion~~ products is 910 ltr/kg, the ~~velocity~~ of detonation

(φ = 1,7) 8400 m/sec, expansion in the Trauzl block is 470 cc.

phlegmatized
The explosive properties of ~~phlegmatized~~ hexogen diminish substantially

with increase in the quantity of phlegmatizer (Bibl.95).

Hexogen is employed to fill small-caliber shells, shaped charges, in

In a
detonators, and in caps. In a mix with aluminum powder or trotyl, it is

employed to fill various types of munitions. Also employed are mixtures of the

following percentage composition:

Trotyl	60	80	20	12.5	50
Hexogen	40	20	78.5	75.0	40
Paraffin	–	–	1.5	–	–
Tetryl	–	–	–	12.5	–
Aluminum	–	–	–	–	10

Hexogen is also employed in so-called plastic high explosives or

explosive putties. A mixture of hexogen and a binder is soft, plastic, and somewhat

blasting,
tacky. These are employed in ~~sapping~~ for example, may be used to cut metal,

to   demolish
bridge girders, blow up tanks, to demolish reenforced-concrete fire points, etc. Mixtures

of this type consist of 88 parts finely-ground hexogen and 12 parts

78%
grease or 78% hexogen and 22% resinous binder consisting of a

nitro derivative of an aromatic hydrocarbon and nitrocellulose.

Section 2. <u>Technology of Hexogen Production (Bibl.45, 47, 63, 86, 96, 97)</u>

During World War II, the production of hexogen attained particularly

large
large scope in Germany, USA, England, and Canada. In the course of the War, hexogen

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production capacities increased sharply, for example, by more than 90-fold in Germany (from 600 tons in 1938 to 56,600 tons in 1944).

In Germany, a total of five methods were employed in hexogen manufacture, of which the major one was the SH method, consisting of nitrolysis of urotropine with concentrated nitric acid. The other ~~methods~~ methods were experimental and actual production of hexogen by those methods was considerably lower than the capacities of the installation.

In England (Bibl.45), development of a method of hexogen production began in 1932, and in 1933 a plant producing 34 kg of hexogen per hour without recovery of the spent acid was already in operation. At the end of 1939, recovery of nitric acid wastes by absorption of nitrogen oxide and concentration of the spent acid was achieved. This made it possible to recycle about 5.5 ton of nitric acid per ton of finished product. In 1941, a plant began to function in the vicinity of ~~bridge washer;~~ Bridgwater producing 90 tons of hexogen per week, and subsequently this figure was doubled. Hexogen was obtained by direct nitrolysis of urotropine by concentrated nitric acid or by the so-called oxidizing method. By 1942, the acetic anhydride method, which is economically much more advantageous, was developed. In the United States and Canada, hexogen was produced by the same methods as in England. The first MX plant, started in the summer of 1941, worked on the basis of a technology borrowed from Britain (Bibl.69). Simultaneously, joint investigations were carried out in the USA, England, and Canada, and the development of a technology for the production of oxygen by the acetic anhydride method (Bibl.69). In February 1942, an experimental plant was put into operation

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for the production of oxygen by the acetic anhydride method in continuous

apparatus, and subsequently (1943), a plant went into operation at which the

spent acid was completely recovered.

Production of Hexogen by the Oxidizing Method (Bibl.60)
English Variant

A technological process for the production of hexogen consists of

three stages: nitration, washing, and drying, performed in separate buildings.

Nitration. At this stage, nitrolysis of urotropine is performed by direct

metering of crystalline urotropine and concentrated nitric acid into a cooled

reaction mixture consisting of the same ingredients. The resultant solution

contains hexogen and various undesirable ~~XXXXXXXXXXXXX~~ byproducts, as well as ~~XXXXX~~

a considerable quantity of unutilized ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXXX~~ nitric acid.

This solution is run into a vessel in which it is diluted with water to

crystallize the hexogen out. The nitro mass is held at high temperature, so

as to ~~XX~~ make it possible for the byproducts ~~XX~~ dissolved therein to decompose.

The residual weak acid is separated from the solid hexogen by continuous

filtration and is mixed with weak acid obtained from absorption columns, ~~XXX~~

before being sent to concentration.

These processes are performed in two or three nitrators and two dissolvers,

arranged in series.

A nitrator (Fig.80) consists of a rectangular vessel of stainless steel

divided by partitions into three sections each having an agitator. In the first

section there are three concentric coils (cooling surface 1.8 m^2). The second

and third compartments have one coil each. The temperature of the nitro mass in

the first and second sections must not be over 25°. In the third section of

the nitrator, hot water circulates in the coil, and the temperature of the

nitro mass is held at 38°, which facilitates increased hexogen yield.

XX Two gas tubes lead from the cover of the nitrator, and the first tube

contains a cylindrical pyrex observation window for examination of the color

of the gases emitted. The appearance of any considerable quantity of nitrogen

oxides warns of the need for immediate XXXX dumping of the nitrator contents

276 into the emergency vat. The covers of the first and second compartments have

apertures through which the urotropine is delivered. A feed XXXXX apparatus for

delivery of nitric acid is provided in the first compartment. A discharge aperture

is provided in the wall of the third compartment.

The feed device for delivery of urotropine is installed in the compartment

above the nitrators. This consists of a double receiving hopper having two

horizontal screw feeds. These are actuated

by gear boxes and meter the urotropine, so

that the second XXXXXX feeder XXXXXX provides

1/4 as much as the first. The speeds may be

regulated so that the total feed is from

57 - 170 kg per hour. The controlled flow

through
of urotropine is sent through the floor XX

troughs into
two XXXXXXXXXXXXXXXXX the first two

worm
compartments of the nitrator, vertical XXXXX

Fig.80 - Appearance of Nitrator

conveyors being employed. The delivery of

nitric acid into the nitrator is through a variable-area flow meter.

A discharge valve is provided in the bottom of the nitrator, through which the nitrator contents XX flow into a tank containing an aqueous urea solution. When the nitro mass is discharged to the solution, considerably less gas is emitted than when it is discharged into pure water. The nitro mixture goes
standpipe
from the nitrator into a XXXXX feeding the diluter.which is located somewhat lower.

The diluters (Bibl.81) are similar to the nitrators in form, but considerably larger (l = 2.6.m; b = 0.6 m; h = 1.1). The useful depth is 0.7 m. Each diluter contains four chambers for mixing, equipped with cooling coils.

The agitators have flat vanes and operate at 195 rpm.

The nitro mass emerges from the diluters through closed troughs and goes to a cooler consisting of three chambers (a principal chamber and two auxiliary chambers). The cold mass flowing from these chambers goes to classifying filters (Fig.82).

At the onset of nitration, the diluter is filled with 55% nitric acid, which is then heated approximately to 100° by XXXXX steam circulating in the coils. Steam delivery is gradually diminished as the nitro mass arrives from the nitrator, and water delivery is turned on. The amount of water provided is such as to cause the concentration of the outgoing acid to be 55%. The temperature of 75° is maintained in the diluter.

The nitrogen oxides, usually XXXXXX liberated in the diluter, are removed from each chamber through a pipes XXXXXXXX joined in a single line, which are

in turn connected to a single manifold leading to a condenser.

The nitro mass goes to the first chamber, in which water for dilution is delivered through the roof by tube. Wash water is used for this purpose. The amount of water delivered is regulated by a variable-area flow meter.

The gas line is equipped with ~~MAIXXAX~~ emergency Venturi-type steam jet feed devices for use in case of a power failure or failure of the fans. The pressure depression in the gas line is held at 12 - 19 mm Hg during the entire operation. Any violation of this ~~depression~~ negative-pressure regimen may lead to filling the building with gas, as each diluter produces up to 6.8 kg NO_2 per hour under normal conditions of operation. Therefore, provision is made for the use of emergency jet feeds for the gas instruments, which may be connected at the building door.

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A sloping gas ~~XXMAX~~ line runs from the building to a barometric condenser, in which the acid condensate is accumulated and from which it is returned to the system, while the non-condensing gas goes to another condenser (diameter 1.8 m, height 3.3 m, containing 706 38-mm stainless steel tubes, 2.4 m long, in three passes, cooled with water ~~IXXXX~~ from without). The condensate is collected at the bottom and ~~returned~~ recycled to the system, and the gas, which by now is cooled to 20 - 30°, proceeds along the stainless steel line leading to absorption columns (Fig.83).

The nitration building has a control panel.

Fig.81 - Appearance of Diluter

The mass of raw hexogen and weak nitric acid go from the cooler through a closed trough to the first filter, where the spent acid is separated 自自自 from the hexogen. The hexogen then goes to a second filter, in which it is washed with water to remove the remaining acid. The acid water is sucked into a sump and is later used to dilute the nitro mass.
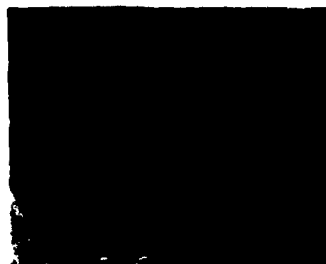
Fig.82 - Appearance of Classifying
Filter

The raw hexogen emerging from the second filter goes to a car (stainless steel) in which it is transported to the washing department. At another plant, the hexogen is washed off the filter by water into a wooden vat equipped with an agitator (500 rpm). The hexogen suspension is pumped from the vat to the washing compartment through a 50 mm tube by means of a steam-jet ejector.

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<u>Washings</u>. Raw hexogen contains a portion consisting of coarse granular

particles which have tb be reduced in size inasmuch as, in the intervals between

the crystals, they contain nitric acid (0.1 - 0.2%). Moreover, there is nitric

278   acid in the wash liquid remaining on the raw hexogen. The purpose of the

technological processes in this stage is to reduce the size of the large

hexogen grains and remove the nitric acid by washing.

A car contining raw hexogen, upon arriving at the wash builuing, is rolled

                                           third
under a steam-jet apparatus, to the suction end of which a XXXXX and a fourth

   hose is
XXXXXXXXXXX fastened. The water is added to the hexogen mass by means of a hose.

The entire mass is picked up by the suction of a steam ejector as the hexogen

softens. Thus, a single woman worker is able to XXXX empty and fill a wagon in

five minutes time.
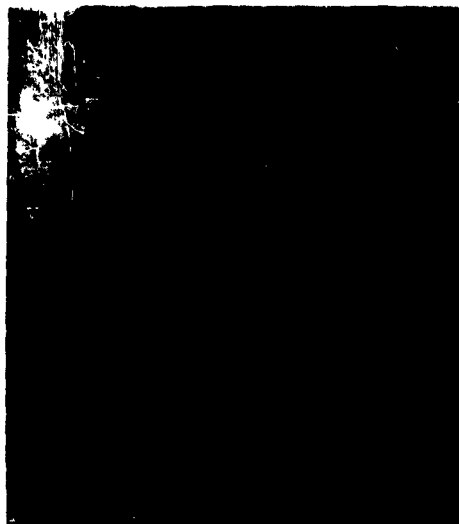
Fig.83 - Appearance of Absorption Apparatus

The suspension is ejected by steam and goes to one of the two stainless

steel mixers, having a rounded bottom 1.2 m in diameter and 2.1 m high. From

these receivers, the mass of water and hexogen, in approximately 3:1 ratio,

to ~~xxxxxx~~ xroller mills

goes by gravity ~~xxxxxx~~ where the grains are crushed. Water is delivered to

the rows simultaneous with the hexogen mass in order to prevent heating should

rollers

delivery be interrupted. The ground mass is raised over the ~~xxxxxx~~ to a 25 mm tube

of stainless steel, to a NXX height of approximately 460 mm, and may be directed

into a vat by means of a rubber hose.

The XXXX vats (Fig.84) are of Columbia pine and are mounted on brick masonry

piers beneath the floor. The height for each vat is 2.5 m, and its diamter 2.4 m.

The bottom slopes toward the discharge aperture, over which a steel-faced valve

is XX located. A similar valve is provided on the wall (1 m from the base) for

decanting purposes. The vat has an agitator. The mass it contains is heated

bubbler,

with XX live steam delivered through a / which fails by 150 mm to reach the bottom

of the vat, and which ends in a slit-like nozzle.

About 2000 kg hexogen is charged into the vat. After the suspension of hexogen

and water has entered the vat, the agitator is XXXX stopped, and the suspension is

given 45 min to settle, subsequent to which acid water is poured into a wooden

thrice

trap via a decanting valve. The mass is washed XXXX with cold XXXX water, and

after water has been run in for a fourth washing, the mass is heated with live

steam to 90 - 100° and held at that temperature for 12 hrs.

After decanting, the moist hexogen is dumped from the vat and sent for

further use.

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It has been suggested that, in order to obtain loose-flowing hexogen, that 0.5 - 5% potassium stearate by weight or other soluble salts of an aliphatic acid containing more than 10 carbon atoms be added to the suspension in warm water, followed by an aqueous solution of $CaCl_2$ or some other water-soluble salt (Mg, Zn, Pb, or Ni).
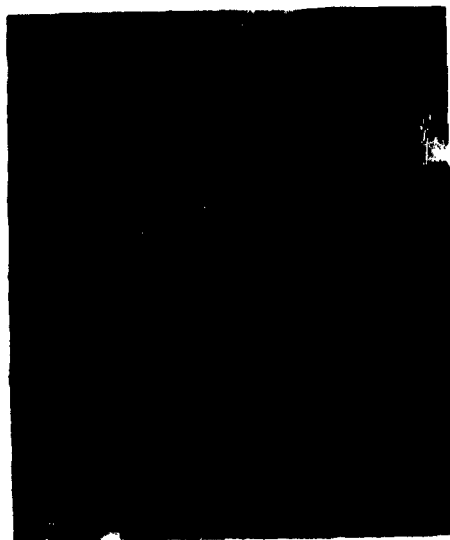
Fig.84 - External Appearance of Washing Vat

<u>Drying.</u>   Hexogen is dried in vacuum-drying desiccators at 60°.

Hexogen to be used to make mixtures with TNT is not dried. Water removal is performed during mixing with the molten TNT.

The amount of initial products required per ton of hexogen is (in tons):

Urotropine 0.83

Nitric acid 8.78

   Of which:

     Returns as spent acid (55% HNO_3) 3.48

Is cracked by absorption system 3.43

Goes to XXX nitrolysis 1.87

H_2SO_4 consumed in concentration of the spent and adsorbed acid 0.49

Consequently, the hexogen yield is 37.7% in terms of formaldehyde, 56.7% in

terms of the amino groups, and 9.7% in terms of nitric acid. The concentration

of the nitric acid employed is 95 - 96%, and the modulus is 10.5.

280   The German Variant

The "SH" method was developed in 1937 by Schnurre (Bibl.49, 65, 86, 98).

As distinct from the English XXX variant, the process is run in batch-type

apparatus and a smaller amount of nitric AA acid, but of higher concentration

(99% HNO_3) is employed for urotropine nitrolysis. Figure 85 presents a diagram

of the technological process for the production of hexogen.

Nitric acid cooled to 0° is charged into nitrator (2), and pre-desiccated

urotropine is slowly added thereto, the temperature being held at not more than

20°. To avoid liquifaction of the urotropine, it is recommended that it be charged

in the form of compressed.balls (Bibl.98). After nitration has ended, the nitrator

contents are emitted into the buffer apparatus, XXXXX from which the nitro mass

passes successively through apparatus (4), (5), (6), (7), and (8), in which the

urotropine undergoes complete nitration. A temperature of 15 - 20° is maintained

in buffer apparatus (3) through (8). Further, the nitro mass goes from buffer

apparatus (8) to stabilization in two oxidizers (principal oxidizer 9 and buffer

oxidizer 10], to which water is delivered simultaneously for dilution. A temperature

of 70 - 80° is maintained in the oxidizer.

Then, the suspension of hexogen in spent acid flows to the cooler (11)
and then goes in sequence through three more coolers (12), (13), (14). Natural
cooling takes place in the first §X three coolers, while in the last the
nitro mass is cooled by water to 20°.

From cooler (14) the nitro mass is discharged into a drum filter (or
centrifuge) 15, the spent acid is drained into a receiver (16), and the hexogen
is washed two or three times with cold water, and then stirred with water in
a mixer (17). In the mixer, the hexogen is mixed with water and the suspension
is sent by centrifugal pump to autoclaves (18) (the pressure in the autoclaves
is 2.5 - 3 atm) in another building, where it is heated to 130 - 140° and held
at that temperature for 4 - 5 hrs.

The rate of removal of acid when hexogen is washed in the autoclave rises
with increasing temperature up to 150°, but remains virtually constant thereafter.
The velocity does not depend upon the relationship between the amount of water
and hexogen (as it does in cooking without an autoclave), but is dependent on
crystal size XMXIXX and is determined primarily by the rate of diffusion of the
acid to the surface of the crystals.

281   When hexogen is washed in an autoclave, hydrolysis of the hexogen may
set in at as low as 140°, and it will reach 0.5% within two hours. When the
temperature is raised to 150°, the rate of hydrolysis rises sharply. The
decomposition of hexogen upon washing proceeds by complete destruction of
the XIXX molecule to form liquids and gases which do not impair the properties

XXX

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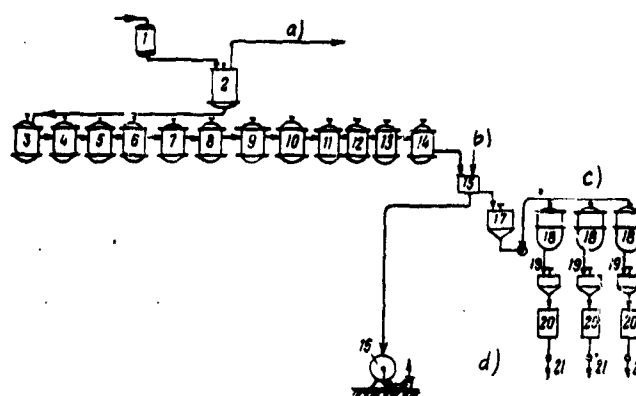
Fig.85 - Diagram of Production of Hexogen by Oxidation Method

1 - Tank for cooling HNO_3; 2 - Nitrator; 3 to 8 - Buffer apparatus to complete nitration; 9, 10 - Apparatus for oxidation; 11 to 14 - Coolers; 15 - Centrifuge; 16 - Receiver; 17 - Mixer; 18 - Autoclaves; 19 - Rectification apparatus; 20 - Filter hoppers; 21 - Sacks

a) Urotropine; b) Water; c) Cooking phase, under pressure; d) Spent acid to concentration

281   of the hexogen: the hexogen is not contaminated by its own decomposition products. (Bibl.91).

Upon conclusion ~~of~~ of the cooking in the autoclave, the mass is cooled to 100°, and drained into a phlegmatization apparatus (19), containing fused synthetic wax colored by Sudan dye. The amount of wax used is such as to cause it to ~~constitute~~ constitute 5% of the hexogen. After the hexogen suspension has been run into the wax, the mass is rapidly cooled to 20° in 30 min and drained to ~~filter~~ filter-hopper (20), where the hexogen is squeezed out to 10% moisture content within two hours. The dried hexogen is emptied into silk sacks and sent to another plant for drying.

The acidity of hexogen after washing on the filter is 0.3 - 0.4%, and after

cooking in the autoclave it is 0.1%. The melting point of the resultant hexogen

is 202°. 0.83 - 0.84 ton Urotropine and 7.1 ton (99%) nitric acid is consumed

per ton of hexogen, of which 5.2 tons are recovered.

The oxidizing method of producing hexogen, yielding a high-quality product,

is quite simple, dependable, and sufficiently safe, ~~but it~~ *although it* has a number of

significant inadequacies. The major ones are the large consumption of concentrated

nitric acid and the low yield of hexogen in terms of formaldehyde (35 - 40% of

the theoretical). The need for twice diluting the acid with water in order to

remove the hexogen also greatly increases the cost ~~XXXXXXXXXXXXX~~ *of concentrating* the spent acid

or recycling. Bearing these shortcomings in mind, the researchers in a number of

countries conducted investigations with the object of developing more perfect

methods of obtaining hexogen. In Germany, during World War II, hexogen was

obtained by other methods as well: the "acetic ~~XXX~~ anhydride" ("KA"), the "white

salt" ("W"), the method based on condensation of formaldehyde with ammonium

nitrate in the presence of BF_3 ("E").

In the United States, England, and Canada, hexogen was obtained by the

acetic anhydride method which proved considerably more effective than the oxidizing

method (Bibl.69).

Producing Hexogen by the "W" Method (Bibl.63, 86)

During World War II, experimental installation operated in Germany at which

hexogen was produced by the highly original "W" method (the sulfaminic acid as

intermediate). A schematic diagram of this installation is presented in Fig.86.

Reaction of ammonia with sulfuric anhydride, which is metered in a ratio

of 1:3, is performed in the condenser (1). This results in the formation of

sulfonate
ammonium imino ~~XXXXXXX~~ and imino disulfonate:

$$SO_3 + 2NH_3 \rightarrow NH_2SO_3NH_4;$$
$$2SO_3 + 3NH_3 \rightarrow NH(SO_3NH_4)_2.$$
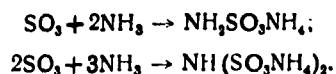
The salt obtained is dissolved in thrice the amount of water and discharged

into vats (2), whereupon calcium oxide is added, in 110% of the theoretically

necessary quantity. The solution is heated by live steam to remove the ammonia,

and it is filtered free of the excess calcium ~~XXXXXXXXX~~ hydroxide on filter (3).

it
The filtrate is received in vat (4), where/is acidified with sulfuric acid

from metering tank (5). In these operations, the following ~~XXXXXXXXX~~ reactions

occur:

$$NH_2SO_3NH_4 + NH(SO_3NH_4)_2 + 2Ca(OH)_2 \rightarrow$$
$$\rightarrow (NH_2SO_3)_2Ca + CaSO_4 + 3NH_4OH.$$
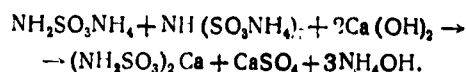
282   When calcium iminosulfonate is acidified, it hydrolyses to form sulfaminic

acid.

potassium
In order to produce/sulfaminate, potassium oxide and ~~XX~~ potassium bisulfate

are run into vat (4) after acidification and agitation:

$$NH_2SO_3H + KHSO_4 + Ca(OH)_2 \rightarrow NH_2SO_3K + CaSO_4 + 2H_2O.$$
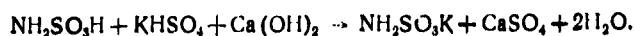
Then, the potassium sulfaminate is filtered on funnel (6) free of the $CaSO_4$.

The filtrate then goes to a vacuum evaporating column (7), where it is vaporized,

and then goes to crystalliser (8) and filter (9). The filtered crystals of

535

potassium sulfaminate go to condenser (10), into which formalin is added from

vat (11). A condensation reaction XX is run at 30°, the pH of the solution being

held at 5. The solution is then steamed in the XXXXXX vacuum vaporizing apparatus (12),

cooled in, crystallizer (13), and the crystals are filtered off on hopper (14). The

potassium cyclotrimethyleneiminosulfonate XXXXXXXX ("white salt") obtained is

dried in desiccator (15).
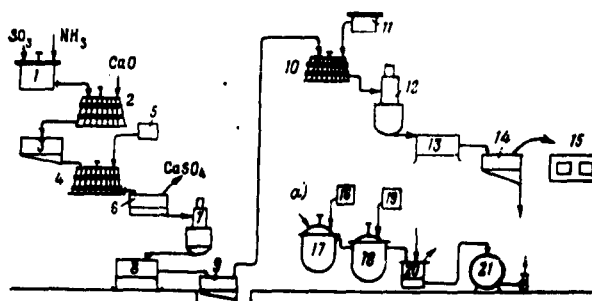
Fig.86 - Diagram of Production of Hexogen via Sulfaminic Acid

1 and 10 - Condensators; 2 and 4 - Vats for decomposition; 3, 6, 9, 14, and

20 - Filter hoppers; 7 and 12 - Evaporation columns; 8 and 13 - Crystallizers;

5, 11, 16, and 19 - Metering tanks; 15 - Dryer; 17 - Nitrator; 18 - Diluter;

21 - Receiver

a) "White salt"

The nitration of "white salt" is performed by a nitro mixture of the

following composition: 80 - 81% HNO_3; 4 - 5% H_2SO_4; 13 - 14% SO_3, and 1 - 2% N_2O_4,

which is delivered from metering tank (16) (the quantity being 1.8 parts by

XXXX weight per 1 par- "white salt") into nitrator (17). The nitro mass goes

from nitrator (17) to diluter (18), into which water is delivered from metering

tank (19) for dilution to a specific gravity of 1.2 - 1.3. Then the hexogen is

filtered XX free of the spent acid on filter (20), and, after first being

washed with water, goes to the final washing and stabilization. The spent

acid is of the following composition: 23% HNO_3; 13 - 14% XXXX H_2SO_4; 10 - 11% $KHSO_4$;

52 - 54% H_2O.

<u>Production of Hexogen by Method "K" (Bibl.63, 86)</u>

In 1936, Knoffler developed a method of producing hexogen called method "K".

Figure 87 presents a schematic diagram of the technology involved in the production

of hexogen by XXXXX this method.

283   Urotropine is nitrated by a solution of ammonium nitrate in concentrated

nitric acid. Nitration is performed in two stages. In the first stage,

urotropine is added to a solution of ammonium nitrate in nitric acid at 20°. This

results in the formation of hexogen and formaldehyde. The latter reacts, in the

second stage, at a temperature of 65 - 70°, with ammonium nitrate and nitric

acid, to form additional hexogen. The mass is then cooled.

The hexogen obtained is separated from the spent acid on a drum filter,

washed with water, and crystallized out of acetone. If necessary, the hexogen

is subjected to phlegmatization.

The spent acid contains a certain amount of formaldehyde, as a consequence

of which it is unstable and cannot be XXXXXXXXX subjected to regeneration.

Therefore, the spent acid is first heated in special apparatus 90 - 95°. This

is accompanied by complete oxidation of formaldehyde XX partial decomposition
                and

of ammonium nitrate. The nitrogen oxides and nitric acid vapors liberated therein

XX   537

Fig.87 – Diagram of Production of Hexogen by Method "K"

1 – First-stage nitrators; 2 – Second-stage nitrators; 3 – Metering tank for nitric acid; 4 – Coolers; 5 – Drum-type vacuum filters; 6 – Washing apparatus; 7 – Acetone collector; 8 – Acetone metering tank; 9 – Dissolver; 10 – Crystallizer; 11 – Filter-hopper

a) Nitration; b) Spent acid; c) Acetone to purification

go to an absorption apparatus. The stabilized nitric acid, containing about 48% HNO_3 and 24% NH_4NO_3 are subjected to distillation in a special apparatus.

The major advantage of the "K" method is a good yield of hexogen ~~150%~~ (60% of theoretical in terms of formaldehyde). Serious shortcomings of the method are: the large ~~XXXXXXX~~/amount of material that have to be processed (more than 14 tons of product per tons of hexogen, which results in a pronounced reduction of the ~~XXXXXXXXXX~~ productivity of the apparatus, and complicates the process), and the very complex process of recovery of the nitric acid and ammonium nitrate.

0.48 - 0.5 ton Urotropine, 4.8 tons ammonium nitrate, and 8.6 tons nitric acid are consumed per ton of hexogen. 3.6 tons ammonium nitrate, and 7.2 tons nitric acid are recovered.

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Production of Hexogen by the Acetic Anhydride Method
German Variant (Bibl.63, 86)

In Germany, two methods of producing hexogen with the use of acetic anhydride have been developed: the "KA" and "E" method.

The "KA" method is a further improvement of the "K" method. The technological process of production by the "KA" method consists of the following operation: 1) making urotropine dinitrate; 2) making ammonium trinitrate; 3) nitrolysis of urotropine dinitrate by ammonium trinitrate in the presence of acetic anhydride at 50 - 60°; 4) filtration of the hexogen free of acids, washing of the hexogen, and stabilization thereof by cooking with water under pressure; 5) drying of the hexogen; 6) regeneration of acetic anhydride and spent acid.

First the dilute spent acid is regenerated by decomposition at 700°. This is XXXXX accompanied by conversion of the acetic acid into monomolecular anhydride-ketene:

$$CH_3COOH \rightarrow CH_2 = CO + H_2O.$$
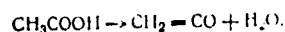
Ketene is a gas that reacts with acetic acid to form acetic anhydride:

$$CH_2 = CO + CH_3COOH \rightarrow (CH_3CO)_2O.$$

The hexogen yield by this method XX attains 75 - 80% of the theoretical in terms of formaldehyde. Shortcomings of the method include production of hexogen of low melting point (not over 192°) and the danger involved in the recovery of spent acetic acid, inasmuch as it contains unstable products.

The products consumed per ton of hexogen are 1.4 ton urotropine, 0.43 ton ammonium nitrate, 0.68 ton (99%) nitric acid, and 2.4 ton acetic ~~anydri~~ anhydride.
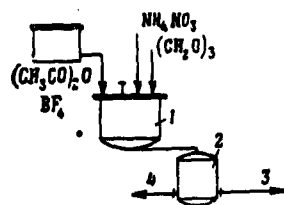
Fig.88 - Diagram of Production of
Hexogen by the "E" Method
1 - Reactor; 2 - Nutsch; 3 - Hexogen
to washing; 4 - Mother filtrate
(to separation of catalyst)

Another method of producing hexogen was developed in 1935 - 1938 by Elbe, and was termed method "E". The initial products are paraformaldehyde, ammonium nitrate, acetic anhydride, and boron fluoride as promoter. Figure 88 illustrates the schematic diagram for the production of hexogen by this method. The process is carried out as follows.

Paraformaldehyde and dry ammonium nitrate are introduced into the acetic anhydride containing boron fluoride (0.4% BF_3) and heated to $60 - 65°$. The hexogen produced is separated from the spent acid ~~ci~~ ~~filter~~. ~~Nutsch~~. The spent acetic acid is distilled and ~~skin~~ again converted to acetic anhydride, which is recycled.

Advantages of the method include the high yield of hexogen (80% of theoretical, computed in terms of formaldehyde) and the use, as the nitrating substance, of ammonium nitrate, which is cheaper than concentrated nitric acid. Shortcomings are the low melting point of the hexogen obtained, as a consequence of the fact that it contains impurities (about 7%), and the danger involved in recovering the spent acid. Other difficulties include the complexity of preparation of paraformaldehyde, and the large consumption of ammonium nitrate and acetic anhydride.

The following
XXXXXXXXXX is the consumption per ton of hexogen: 0.63 - 0.635 ton

paraformaldehyde, 1.8 ton ammonium nitrate, 5 - 5.1 ton acetic anhydride, and

0.019 ton boron fluoride. The hexogen obtained contains up to 6% oxygen.

285   The Canadian Variant (Bibl. 45, 69, 96)

In Canada, the United States, and England, work was done jointly in the

development of an **XXXXXX** acetic anhydride method of producing hexogen (Bibl.69).

In October 1940, Ross and Shisler (Bibl.72) observed that reaction of

nitrate
formaldehyde and ammonium **XXXXXXXX** with acetic anhydride yields hexogen:

$$3CH_2O + 3NH_4NO_3 + 6(CH_3CO)_2O \cdot \cdot (CH_2NNO_2)_3 + 12CH_3COOH.$$
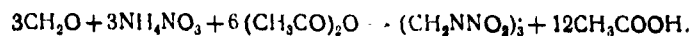
This reaction does not require the use of urotropine or large amounts of

nitric acid. The new method employs acetic anhydride, which these countries

were in a position to produce in large quantities (Bibl.69).

The investigations were begun in Canada by a group working under the

leadership of Bachman of Michigan University, and were tested at Canadian plants.

Bachman's work showed that Ross' reaction could be combined with a nitrolysis

products
reaction so as to get the best results. Inasmuch as the initial **XXXXXX** of the

Ross reaction - formaldehyde and ammonium nitrate - come into being as waste of

the nitrolysis reaction, further addition of ammonium nitrate and acetic acid

to the XX nitro mass had to result ~~to~~ the formation of an added molecule of hexogen.

This was confirmed by experiment.

The equation for the combined process suggested by Bachman (Bibl.67, 68)

may be depicted as follows:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2(CH_2NNO_2)_3 + 12CH_3COOH.$$
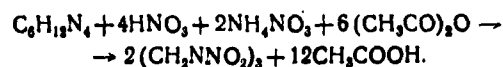
In February 1942, a DuPont Plant began operations to produce hexogen

under XXXXXXXXXXXXXXXXXXXXX this combined method. In May 1942, production

of hexogen by the combined method was begun at an Eastman Plant. At this plant,

the process was performed in continuous apparatus, and the spent acid was

recovered in acetic anhydride, and then again employed to produce hexogen.

The acetic anhydride method of producing hexogen, which resulted in twice the

yield of the nitrolysis process, proved considerably more economical for England,

Canada, and the USA (which had adequate supplies of acetic acid and acetic

anhydride) (Bibl.69).

                                    the

The technological process for/production of hexogen by the Bachman-Ross method

is as follows.

                                in
First, solutions of urotropine XXX glacial acetic acid and of ammonium

nitrate in 97% nitric acid are prepared. The solutions are heated to 40°, and

the acetic anhydride is simultaneously heated to 60°. The prepared solutions are

slowly run into the acetic anhydride. Run-in of the components is performed

at 70 - 75°. Upon completion of run-in, the mixture is held for 15 - 20 min at

the same temperature, and then 640 moles of water heated to 40° is added to the

nitro mass (Bibl.45).

The generation of the acetic acid is performed by adding sulfuric acid to

                          processes.
the spent acid in two XXXXXX The first portion consists of 5 - 10% of the weight

of the spent acid, whereupon the mass is heated to 100°. The second portion is

15 - 40%. The mixture is subjected to distillation at 120 - 140° for the purpose

of driving off the acetic acid (Bibl.99). It is recommended that the spent acid

first be treated with NH_3 in order to reduce the HNO_3 content to 1% (Bibl.100).

It is suggested that the nitro mass obtained be diluted with water at 90 - 100°, and that after separation of the hexogen, it be subjected to distillation XDBDBG to drive off the acetic acid (Bibl.101).

Safety Procedure in Hexogen Manufacture

In addition to the XX safety rules common to the XX production of all explosives, the high sensitivity of hexogen to mechanical effects must be borne in mind. All hexogen shops are dangerous in terms of explosion and fire, except for the urotropine production shop, where the only danger is that of fire.

286

The harmful physiological effects of hexogen dust, urotropine dust, as well as of nitrogen oxides and nitric acid must be noted.

Buildings in which hexogen are produced, and the apparatus in which the process occurs have to be provided with the appropriate devices to assure safe operation.

In England (Bibl.60), the production of hexogen is carried out in a number of small buildings separated by substantial distances. All the buildings are surrounded by embankments and connected by special corridors open to the side. The roofs of these corridors are of asbestos cement and serve solely for protection against XXXX rain. The floors both of the buildings and of the corridors are of asphalt. The walls are cement. The buildings have lightening rods, and the apparatus is provided with special equipment to remove static electricity.

In work in the shop, blows of metal against metal are wholly ruled out.

Particular attention is directed at the cleaning of the plant before repair.

Solidify explosive is cleaned only with wooden equipment, the cleaning is performed

very carefully, and is observed by a technologist. ~~IMM~~ When units have to be

heated or repaired by welding, a technologist checks them out by test burning.

To do this, small one-man steel shelters, with apertures for the hands, and

viewing slits were employed. The burner has a handle ~~XXXXXXX~~ $\overset{1.8 \text{ m}}{\text{long}}$.

~~NX~~ Although it contains some acid or water, hexogen in the various stages

of production is none the less highly sensitive to mechanical effects.

However, the major measure for prevention of fires ~~XX~~ and, particularly, of

explosions, in hexogen production, is strict adherence to the technological

procedures.

In the nitrolysis process, exothermic ~~HMMXXXXXX~~ reactions occur in the

stage of nitration. Even ~~XMMNX~~ when the violation of the ~~XMMNXXMXX~~ technical

process is comparatively minor, these reactions readily lead to ejection of the

nitro mass from the apparatus, or flare-up. It is at this stage that concentrated

nitric acid is employed, contact of which with urotropine or with foreign

organic substances in the absence of agitation readily induces a vigorous reaction

and ignition.

In production, urotropine may ~~MX~~ catch fire in the charging hopper or $\overset{on}{\wedge}$ the

feed conveyor under the influence of nitric acid fumes or spatter. Therefore,

careful observation of the condition of these portions of the ~~XMMXM~~ apparatus,

~~MMM~~ and periodic cleaning thereof is essential.

It must be borne in mind that accidents may occur, in the process of

stabilization of the spent acid, not only at very high, *but t* at *low* reaction

temperature. At low temperature $(40 - 45^{\circ})$, the oxidation process goes

considerably more slowly, as a consequence of which unoxidized impurities MX

accumulate in the nitro mass. This may MM give rise to the *α* vigorous reaction

with ejection of the nitro mass. The degree of dilution of the nitro mass by

water has the same effect upon the oxidation process.

Taking the foregoing into consideration, it is necessary carefully to

monitor the hexogen production process. Moreover, the most reliable type of

monitoring, guarantee*w'z* the safety of the process, is automatic monitoring with

automatic regulation of the process.

When hexogen is produced by the acetic MMIM anhydride method, the following

has to be borne in mind.

Acetic anhydride and acetic acid may form explosive mixtures when mixed with

nitric acid or ammonium nitrate solution in nitric acid in particular ratios.

A mixture with a zero oxygen balance may be obtained when one part acetic

anhydride by weight is mixed with two parts nitric acid. The greater the amount

of nitric acid in the mixture, the more dangerous the mixture will be (Bibl.99).

Mixtures containing 20 parts acetic anhydride by weight per part nitric acid by

weight are deemed to be safe in terms of explosion.

287   When hexogen is obtained by this method, the nitric acid content in the

nitration mass is only 3%, whereas the MMMIII acetic anhydride content may be

up to 7%, and acetic acid up to 85%. Consequently, from the viewpoint of formation

of explosive mixtures, the reaction mass is sufficiently safe. Danger may arise only if very extreme deviation from the metering occurs, when the anhydride and nitric acid ratios reach dangerous limits. The possibility of this kind of violation has to be ruled out by automatic metering and automatic monitoring. In this connection, the storage for nitric acid and the solution of ammonium nitrate in nitric acid should be set up in a separate building, isolated from the building where the anhydride, acetic acid, and spent acid are stored, so as to rule out the possibility that these components may come into contact.

Transportation of the acetic anhydride and acetic acid, nitric acid, and solution of ammonium nitrate in nitric acid must be separate, so as to eliminate the possibility of mixture of these components, which might result in fires and explosions.

In the building itself, the metering tanks and devices must be arranged so that the components capable of reacting with each other are unable to come into contact outside the reactor.

When the equipment is stopped without emptying the apparatus, it is necessary to eliminate the possibility of accidental entry of nitric acid or the ammonium nitrate in nitric acid solution into the apparatus by virtue of wrong functioning of the locking equipment for incomplete closing thereof.

When the work is in progress, it must be borne in mind that acetic anhydride and acetic acid fall into Class II of readily-flammable liquids. Their parameters are indicated in Table 87.

Table 87

a)	b)	c)
Acetic anhydride	43—45	385
Acetic acid	40	566
Benzene	—12+10	490
Acetone	—18+2	500
Dichloroethane	14+21	413

a) Component; Flash point, $^{\circ}C$; c) Temperature of spontaneous combustion, $^{\circ}C$

Section 3. Hexogen Analogs

Cyclotetramethylenetetranitroamine ~~ОХУІЖХ~~ (octogen)
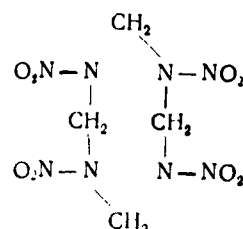
apparently is not yet in use at the present time, inasmuch as both its

chemical properties and, even more so, its explosive properties approximate those

of hexogen very closely, while the cost of manufacture is substantially higher.

octogen

288 ~~ОХУЖЕН~~ may be obtained from the same raw materials as hexogen, but the yield is

lower (Bibl.55,76,102).

Octogen
~~ОХУЖЕН~~ is of ~~ІНІІЖНІІІ~~ interest as a possible admixture to hexogen (up to 10%)

anhydride
obtained by the acetic ~~НУДЖХЕН~~ method. Therefore, ~~ХХ~~ it is necessary to know its

it is
properties, as well as the conditions of its formation, when/undertaken to produce

hexogen. This is particularly important in terms of safety procedures, inasmuch as

octogen
~~ОХУЖЕН~~ ~~ЖХХ~~ has four polymorphic forms, of which only one, the β-form, is stable. The

need to remove the unstable and more sensitive isomers of ~~octogen~~ octogen creates further

difficulties in the purification of hexogen produced by the acetic anhydride method.

Octogen is a solid crystalline light product. When slowly crystallized out of

octogen
acetone,/is obtained in the form-of-large transparent crystals of rhombic shape. The

product purified by recrystallization from acetone has a melting point of 276'- 277°

(decomposes upon fusion). Table 88 presents some of the properties of octogen.

Table 88

Property	Polymorphic Form of Octogen			
	α	β	γ	δ
Specific gravity	1.96	1.87	1.82	1.77
Relative sensitivity to shock (180 in the case of hexogen)*	60	325	45	75
Stability (at room temperature)	Metastable	Stable	Metastable	Labile

*The higher the value, the lower the sensitivity.

Octogen is not soluble in methyl or ethyl alcohols, in benzene, toluene, xylene,

or ethyl ether. It is ~~MMX~~ poorly soluble in dichloroethane, aniline, nitrobenzene,

and dioxane. Its solubility in water at 15 - 20° is about ~~XXXX~~ 0.003% and at 100°

in
about 0.02%. The solubility of ~~XXXXXXXXX~~ octogen ~~XXX~~ various solvents is illustrated

in Table 89

Table 89

Temperature, °C	Solubility of Octogen, %			
	Acetone	Butylacetate	Aniline	Mononitro-toluene
22	2,10	1,14	—	—
27	2,65	—	0,35	—
37	3,52	—	—	—
44	4,0	3,38	—	0,89
56	4,13	—	0,49	1,23
60	—	0,57	—	—
68	—	—	0,67	—
78	—	—	0,89	—
83	—	—	1,05	—
90	—	—	1,19	—
99	—	—	1,38	—
104	—	0,77	1,61	1,60
122	—	0,88	2,09	1,98

The curve of solubility of octogen in acetone is ШКЖ shown in Fig.89.

When octogen is processed with a solution of alkali in aqueous acetone solution,

hydrolysis occurs at a rate less than the rate of hexogen hydrolysis (the activation

energy of the hydrolysis of hexogen is 14 kcal/mole,

and that of octogen is 25 kcal/mole). This difference

in the rates of hydrolysis has been employed (Bibl.90)

for analysis of the octogen content of hexogen. The

accuracy of determination is within $\pm 0.2\%$, thanks to the

Fig.89 - Solubility of Octogen

and Acetone

a) Octogen dissolved

process sequence. Water, 1% solutions of nitric or

sulfuric acids virtually do not decompose octogen

when boiled for 6 hrs. Light does not affect the

octogen.

The stability of octogen is the same as that of hexogen. A manometric specimen

of octogen run for 5 hrs at 166 - 167° shows a rise of 32 - 39 mm in pressure, while

that of hexogen shows a rise of 39 - 40 mm.

Table 90 shows the explosive properties of octogen when XX compared with those of

hexogen. It follows from the data presented that there is virtually no difference

between octogen and hexogen in terms of explosive properties.

Table 90

Property	Hexogen Obtained by the		Octogen
	Oxidizing Method	Acetic Anhydride Method	
Brisance due to Kast when Δ = 1.52, mm	4.5	4.3	5.2
Expansion in lead bomb, cc	440	481	486
Shock sensitivity at p = 10 kg and h = 250 mm, in % complete explosions	96	84	84
Flash point, °C	275	-	2891

In studying the mechanism of hexogen formation reactions by the acetic anhydride method (Bibl.75, 76) 汊 octogen wasobtained, and the conditions of its formation were determined. Epstein and Winkler (Bibl.76) succeeded in getting a 40% yield of 以以以 octogen (in terms of urotropine) when they treated urotropine with a mixture of nitric acid and acetic acid, and ammonium nitrate.

The process is performed by preliminary mixing of the prepared solutions of urotropine in acetic acid and ammonium nitrate and nitric acid with acetic anhydride, with the following molar relationship among the components

$$C_6H_{12}N_4 : NH_4NO_3 : HNO_3 : (CH_3CO)_2O = 1:2:4:7.$$
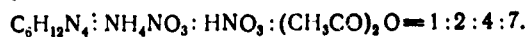
The yield of octogen is 40% in terms of methylene groups. The reaction 汊 apparently goes in accordance with the following equation:

$$2(CH_2)_6N_4 \cdot 2CH_3COOH + 4NH_4NO_3 \cdot 2HNO_3 + 12(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2(CH_2NNO_2)_4 + 28CH_3COOH.$$
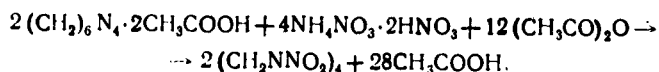
octogen
McKay, Richmond and Wright (Bibl.76) obtained 汊汊汊 by 汊X treating 汊汊汊汊 dinitropentamethylenetetramine with concentrated nitric acid at 10°. These studies have been set forth in greater detail in Sections 1 and 2.

Bachman (Bibl.74) developed a method of producing octogen by the action of a mixture of strong nitric acid (2.2 parts), glacial acetic acid, and acetic anhydride

(6.5 parts) at $15 - 30^\circ$ upon urotropine. Under these conditions, about 20% dinitropentamethylenetetramine is obtained. Nitrolysis of this product at $60 - 65^\circ$
and
by nitric acid in the presence of ammonium nitrate,/nitrogen anhydride results in the formation of octogen, with a yield of about 80% in terms of the dinitropentamethylenetetramine.

Cyclotrimethylenetrinitrosoamine (Bibl.63, 103, 104) is a homolog of hexogen.

It was first obtained in 1888 by Meyer by rapid mixing of a concentrated solution of sodium nitrite with an aqueous urotropine solution containing excess (computed against the nitrite) hydrochloric acid (Bibl.103), performed at low temperature. His formula is:
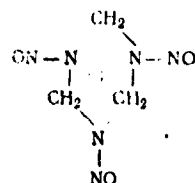
The product may be obtained easily by rapidly running an aqueous ~~XXXXXXXXXXXXXXXXX~~ hexamethylenetetramine solution into an aqueous sodium nitrite solution (5 moles $NaNO_2$ per 1 mole $C_6H_{12}N_4$) and weak nitric acid, in which case the temperature has to be low (0 - 5°), and the pH of the medium has to equal unity (Bibl.49.). A reduction of the acidity of the medium *shifts* ~~the reaction~~ the reaction in the direction of formation of dinitrosopentamethylenetetramine. The initial products may also be formaldehyde and ammonia (Bibl.103). When sodium nitrite is added to an aqueous solution of formaldehyde and ammonia, cyclotrimethylenetrinitrosoamine comes down virtually quantitatively (Bibl.105).

Cyclotrimethylenetrinitrosoamine is a yellow crystalline substance melting at 105°. Its solubility at 15° in 100 gm acetone is 33.4 gm, whereas in methylalcohol it is 2.35 gm, and in acetic acid (100%), it is 5.3 gm. Mineral acids decompose cyclotrimethylenetrinitrosoamine even in ~~XXXXX~~ the cold, while pure acetic acid does not induce decomposition even when heated to 100°. The product is very sensitive to the effects of light (particularly the ultraviolet portion thereof), which sharply reduces its stability (Bibl.103). The reduced stability is also due to the presence

of impurities: nitrous acid and dinitrosopentamethylenetetramine.

Cyclotrimethylenetrinitrosoamine has been proposed by the German Vazag Co. as an explosive the production of which does not require strong nitric acid. However, its comparatively low chemical stability has been an obstacle to its introduction (Bibl.106). Stability may be increased by recrystallization from methyl alcohol or acetone (Bibl.103).

In its explosive characteristics, cyclotrimethylenetrinitrosoamine approximates TNT, as is evident from Table 91.

Table 91

Property	Cyclotrimethylene-trinitrosoamine	Hexogen	TNT
Melting point, °C			
Density, gm/cm³	105	203	81—82
·Velocity of detonation, m/sec	1,53	1,65	1,60
	7500—7800	8300	6850
Brisance, in mm	4,7	5,9	4,2
Fugacity, in cc	386	489	309
Volume of gaseous products, in ltr/kg	853	853	685
Heat of explosion, in kcal/kg	900	1326	1085
	24	16	24
Shock Sensitivity: 10 kg weight does not induce explosion when dropped from an elevation of, in cm			

Trimethylenetrinitrosoamine is an expensive and rather powerful brisant explosive of low sensitivity to shock. A shortcoming is the low chemical stability.

Brockman and Downing (Bibl.82, 107) obtained chemically pure hexogen by treating this product with concentrated nitric acid, and on the basis thereof, have developed a method for producing hexogen free of impurities.

C. Nitroamines of the Aliphatic Series

Section 1. Ethylene-NN'-dinitroamine (EDNA)

Ethylene-NN'-dinitroamine (EDNA or Haleite) was obtained in 1888 by the nitration

of ethylene urea by mixed sulfuric and nitric acid (Bibl.108). The formula is

$$CH_2 — NH — NO_2$$
$$CH_2 — NH — NO_2.$$
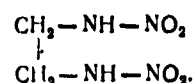
During World War II, methods of producing this substance, termed Haleite was

studied, and in 1943, industrial-scale production began. Haleite was employed for the

same purposes as tetryl. Its advantage over tetryl is higher explosive properties and

synthetic raw materials. Moreover, according to American data (Bibl.109), the

cost of production of Haleite is considerably lower than that of tetryl.

Ethylene-NN'-dinitramine consists of white crystals of rhombic shape. Its

specific gravity is 1.75, and its melting point 175 - 176°. It is not hygroscopic, is soluble in nitrobenzene, dioxane, alcohol, and boiling water, but insoluble in ether.

Solubility at various temperatures in water and ethyl alcohol are illustrated in Table 92.

Table 92

a)	b)	
	c)	d)
25	0,3	1,25
50	1,25	3,45
75	4,95	10,1
95	16,4	—

a) Temperature, °C; b) Solubility, gm of ethylene-NN'-dinitramine (in 100 gm solvent); c) Water; d) Ethyl alcohol 95%

Ethylene-NN'-dinitramine has acid properties and can produce salts with potassium,

silver, and tin. The silver and tin salts are very sensitive to mechanical action.

In alkaline solution, ethylene-NN'-dinitramine is a stable compound, but in

neutral and acid medium it decomposes to form ethylene glycol, acetaldehyde, and nitrous

oxide:

$$2 \begin{array}{c} CH_2 — NHNO_2 \\ | \\ CH_2 — NHNO_2 \end{array} \xrightarrow{-2N_2O} 2 \begin{array}{c} CH_2OH \\ | \\ CH_2NH \cdot NO_2 \end{array} \xrightarrow{-2N_2O} \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + C\!\!\begin{array}{c} O \\ \diagup\!\!\diagup \\ \diagdown \end{array}\!\! H + H_2O.$$
$$CH_3$$
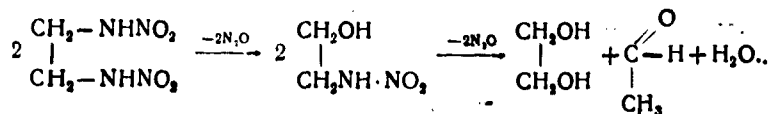
Decomposition is accelerated with rise in temperature and strength of acid.

The dry product virtually does not ███████ decompose, but the moist product starts ███ to decompose at temperatures in excess of 50°. The decomposition products, as well as the impurities, catalytically accelerate decomposition.

The explosive properties of ethylene-NN'-dinitramine are as follows (Bibl.110, 111): flash point 180°, heat of explosion 1276 kcal/kg, volume of gaseous explosion products 908 ltr/kg, velocity of detonation 7750 m/sec (at a density equal to 1.55).

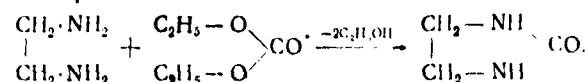Production of ethylene-NN'-dinitramine (Bibl.112, 113). Inasmuch as technical
                                                        a   direct nitration
ethylenediamine is obtained in the form of/60 - 65% aqueous solution, ████████████████ thereof by the action of nitric acid leads IX solely to the formation of a chemically

unstable salt readily soluble in water. Therefore, ethylene-NN'-dinitramine is obtained by nitration of the acyl or ████ formyl derivatives of ethylenediamine.

In the USA, this product was obtained in a ████████ two-stage process industrially (Bibl.109, 114). The essence of each of the two stages is the following: in stage one, the mixture of aqueous ethylenediamine and ███████ diethyl carbonate solution was heated in an autoclave for 4 - 5 hrs at 170 - 190°. The process results in the formation of ethylene urea:

$$\begin{array}{c} CH_2 \cdot NH_2 \\ | \\ CH_2 \cdot NH_2 \end{array} + \begin{array}{c} C_2H_5 - O \\ \diagdown \\ C_2H_5 - O \diagup \end{array} CO \xrightarrow{-2C_2H_5OH} \begin{array}{c} CH_2 - NH \\ | \\ CH_2 - NH \end{array} CO.$$

Water, alcohol, and excess unreacted substances are ██ driven off, and the ethylene urea, obtained in the molten state, is discharged into a drip pan and, after solidification, either crushed to small pieces, or granulated, toward which end the melt is not allowed to solidify, but is run into cold water. The ethylene urea thus obtained has a melting point of 132 - 132.5°, and its yield is about 60% of theoretical.

In the second stage, the ethylene urea is nitrated at 10° by a mixture of nitric and sulfuric acid consisting of 74% H_2SO_4, 15.4% HNO_3 and 10.6% H_2O (Bibl.109, 115). Subsequently, the mixed acid was replaced by 98% HNO_3 (Bibl.109):

$$\begin{array}{c} CH_2-NH \\ | \qquad\qquad \diagdown CO \\ CH_2-NH \diagup \end{array} \xrightarrow[-2H_2O]{+2HNO_3} \begin{array}{c} NO_2 \\ | \\ CH_2-N \\ | \qquad\qquad \diagdown CO. \\ CH_2-N \\ | \\ NO_2 \end{array}$$
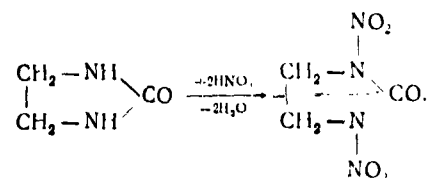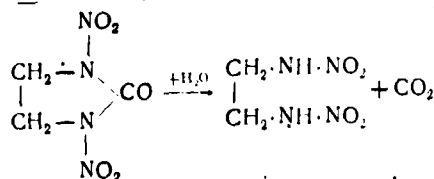
The solution obtained is run into ~~glacial~~ ice water. Crystals of NN'-dinitroethylene urea come down. Due to hydrolysis, precipitation is incomplete. The crystals are filtered off and washed, first in cold and then in warm water (50°).

In the laboratory, nitration is performed more conveniently with nitric anhydride in inert solvent (chloroform) at a temperature of 20 - 30°. The reaction goes rapidly and almost quantitatively. The reaction product is not soluble in chloroform and comes out of solution as it forms. The yield is about 90% of theoretical.

NN'-Dinitroethyleneurea is a crystalline product with a melting point of 211—212°. When boiled with water, it decomposes into CO_2 and ethylene-NN'-dinitramine:

$$\begin{array}{c} NO_2 \\ | \\ CH_2-N \\ | \qquad\qquad \diagdown CO \\ CH_2-N \\ | \\ NO_2 \end{array} \xrightarrow{+H_2O} \begin{array}{c} CH_2 \cdot NH \cdot NO_2 \\ | \\ CH_2 \cdot NH \cdot NO_2 \end{array} + CO_2.$$

Because of significant shortcomings in the method described (low yield of the intermediate product —ethyleneurea, and the need to run a long reaction under pressure), a large number of researchers in the USA engaged in a search for other ways of producing ethylene-NN'-dinitramine. The most interesting of these methods is the following:

292   An aqueous solution of ethyelenediamine XX is heated with acetic XXX anhydride.

Three or four moles of acetic anhydride are taken per mole of ethylenediamine.   Acetic

anhydride also serves as a dehydrator.   The acyl derivative obtained is nitrated with

293   98% nitric acid in the presence of acetic anyhydride at a temperature of $0 - 5^{\circ}C$.   At

the conclusion of nitration, the nitromass is diluted with water to a concentration of

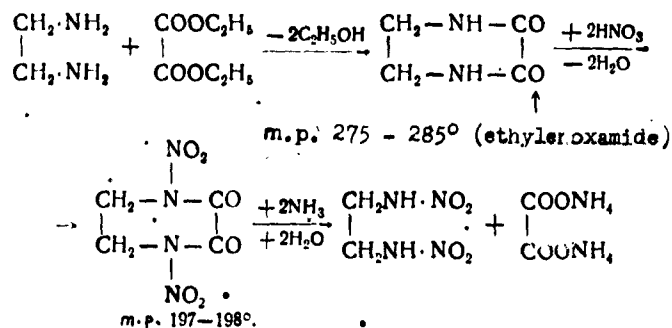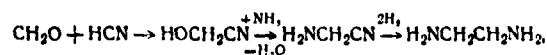$30 - 40\%$ in terms of acetic acid.   The crystals that come down as this occurs are

filtered off and washed with cold water:

$$\begin{matrix} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{matrix} + (CH_3CO)_2O \xrightarrow{-H_2O} \begin{matrix} CH_2NHCOCH_3 \\ | \\ CH_2NHCOCH_3 \end{matrix} \xrightarrow[-2H_2O]{+2HNO_3}$$

$$\xrightarrow{} \begin{matrix} NO_2 \\ | \\ CH_2-N-COCH_3 \\ | \\ CH_2-N-COCH_3 \\ | \\ NO_2 \end{matrix} \xrightarrow[+2H_2O]{+2NH_3} \begin{matrix} CH_2NH\cdot NO_2 \\ | \\ CH_2NH\cdot NO_2 \end{matrix} + 2CH_3COONH_4.$$
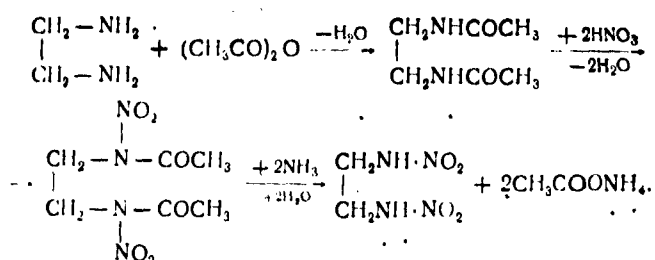
The nitration product is subjected to hydrolysis at room temperature by the action

of 11-- 15% NH$_3$ solution.   The low stability of ethylenediamine significantly reduces

the advantages of this method.   Replacement of ethylenediamine by ethyleneoxamide

renders the method more advanced, inasmuch as the latter has greater stability.(it does

not decompose upon nitration with 98% nitric acid or mixed sulfuric and nitric acid)

(Bibl.112, 115).   The chemistry of the product is as follows:

$$\begin{matrix} CH_2\cdot NH_2 \\ | \\ CH_2\cdot NH_2 \end{matrix} + \begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} \xrightarrow{-2C_2H_5OH} \begin{matrix} CH_2-NH-CO \\ | \quad\quad | \\ CH_2-NH-CO \end{matrix} \xrightarrow[-2H_2O]{+2HNO_3}$$

m.p. 275 - 285° (ethyleroxamide)

$$\xrightarrow{} \begin{matrix} NO_2 \\ | \\ CH_2-N-CO \\ | \quad\quad | \\ CH_2-N-CO \\ | \\ NO_2 \end{matrix} \xrightarrow[+2H_2O]{+2NH_3} \begin{matrix} CH_2NH\cdot NO_2 \\ | \\ CH_2NH\cdot NO_2 \end{matrix} + \begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix}$$

m.p. 197—198°.

293   In the course of improving the production of ethylene-NN'-dinitramine, a cheaper

method was developed, in the USA, for producing ethylenediamine from formaldehyde and

hydrogen cyanide in accordance with the mechanism

$$CH_2O + HCN \rightarrow HOCH_2CN \underset{-H_2O}{\overset{+NH_3}{\longrightarrow}} H_2NCH_2CN \overset{2H_2}{\longrightarrow} H_2NCH_2CH_2NH_2,$$

and nitration of ethyleneurea began to be performed with concentrated nitric acid.

Ethylene-NN'-dinitramine was obtained XX on apparatus for the production of

tetryl, and the yield of ethylene-NN'-dinitramine was three times greater, and the

cost considerably less than the cost of tetryl (Bibl.109).

Section 2. <u>Nitroguanidine (Bibl.116)</u>

Nitroguanidine was first obtained in 1877 by the action of concentrated nitric

or sulfuric acid on XX guanidine nitrate. In industry, it is obtained by dehydration
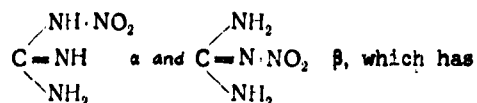
of guanidine nitrate by sulfuric acid.

294   Despite the comparatively high explosive characteristics it displays,

nitroguanidine is not used as an explosive by itself. During World War II, it was used

as a component of nitroglycerine and nitrodiglycol powder instead of dinitrotoluene.

There are many proposals for the utilization of nitroguanidine as a component of

explosives.

Nitroguanidine apparently has a big future, inasmuch as its production is based on

cheap raw materials: lime, coke, nitrogen from the air, ammonium nitrate, and sulfuric

acid. Moreover, its production is related to that of a fertilizer - calcium cyanamide,

from which guanidine nitrate, which is the starting product for the production of

nitroguanidine, is obtained.(Bibl.117).

Nitroguanidine is the starting product for the production of tetrasene which is an

XXXXX

initiating explosive.

Nitroguanidine exists in two tautomeric crystalline forms (Bibl.118)

$$C\begin{cases} NH\cdot NO_2 \\ = NH \\ NH_2 \end{cases} \alpha \quad and \quad C\begin{cases} NH_2 \\ = N\cdot NO_2 \\ NH_2 \end{cases} \beta, \text{ which has}$$

identical melting points of the order of 232 - 250° (melting with decomposition).

The α-form is obtained by the usual method of dehydration of guanidine nitrate:

the action of sulfuric acid followed by decantation in water. This causes the product

to crystallize out of the water in the α-form (long elastic needles that remind one

of loosened asbestos).

The β-form is obtained in part upon dehydration of guanidine nitrate in the

presence of ammonium sulfate. These forms are separated by means of a difference in

their solubility in water. In the range of 25 - 100°, the β-form is more soluble than

the α-, and at temperatures of less than 25° and more than 100°, the α-form is

more soluble. Crystals of the β-form, recrystallized from water, are plate shaped.

If crystals of the β-form are dissolved in sulfuric acid, and the solution is decanted

into water, crystals of the α-form (Bibl.119) are obtained.

The specific gravity of nitroguanidine is 1.72.

Its solubility in water, organic solvents, sulfuric, and nitric acid is illustrated

in Tables 93 - 95.

Table 93

a)	b)
Ether	0,04
Ethyl alcohol	0,18
Acetone	0,19
Methyl alcohol	0,50
Pyridine	1,75
Water	0,27
"	1,18 *at* 50°
"	10,36 *at* 100°

Table 94

a)	b)
5	0,6
10	1,6
20	3,0
50	5,8
87	22,3

a) Solvent; b) Solubility, gm, at 20°, of Nitroguanidine (in 100 gm solvent)

a) Concentration of HNO_3, %; b) Nitroguanidine solubility at 20°, gm (in 100 gm acid)

The best solvent for crystallization of nitroguanidine is water, but the crystals

have the appearance of cotton wool

that come down are fitted and are of very low gravimetric density (0.2 - 0.3). The gravimetric density of crystals is increased by adding colloidal substances (polyvinyl alcohol, gelatin, etc.) or substances that neutralize salts (urea nitrate, ammonium sulfate, etc.) to the solution.

Depending upon the conditions of crystallization, the gravimetric density fluctuates from 0.2 - 0.8.

Nitroguanidine forms eutectic mixtures (Bibl.115), shown in Table 96, with a number of substances.

Table 95

a)	b)	
	0	25
45	5,8	10,9
40	3,4	8,0
35	2,0	5,2
30	1,3	2,9
25	0,7	1,8
20	0,4	1,0
15	0,3	0,5

a) Concentration of H_2SO_4, %;
b) Nitroguanidine solubility, gm, at temperature, °C (in 100 cc acid)

Table 96

| a)	b)	c)
NH_4NO_3	20	131,5
Guanidine nitrate	41	166,5
17.5% guanidine nitrate and 25.5% NH_4NO_3	57	113,2

a) Component; b) Amount of nitroguanidine in eutectic, %; c) Melting point

of eutectic, °C

The following is the structural formula of nitroguanidine (Bibl.120, 121, 122, 123):
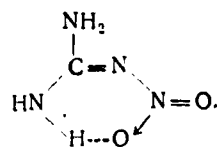
Nitroguanidine XX has weakly basic properties. Under normal conditions it is a

stable compound. In hot water it hydrolizes in part:

$$NH_2-C-NHNO_2 \rightarrow NH_3 + NO_2HN-CN \quad \text{(nitrocyanamide),}$$
$$\underset{NH}{\|}$$
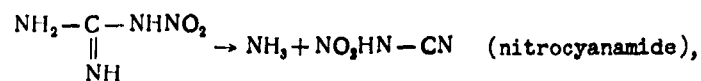
and, upon boiling, hydrolysis goes very intensively to formation of gaseous products:

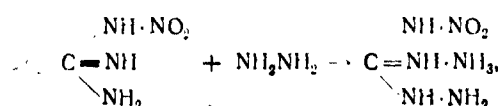$$NH_2-C-NHNO_2 \xrightarrow{+H_2O} 2NH_3 + N_2O + CO_2.$$
$$\underset{NH}{\|}$$

its
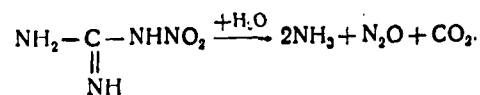
Weight losses of nitroguanidine when/solutions are heated in an autoclave at

120° for 48 hrs are (in %):

in acid medium (pH = 3.9 - 6). 0.19

in neutral medium (pH - 7 ↔ 9) 0.51

in alkaline medium (pH = 8 - 9) 2.74

(the change in pH in the course of heating is shown in parentheses). As these data

indicate, nitroguanidine is more stable in an acid medium.
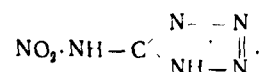
Nitroguanidine results in an explosive substance in an aqueous hydrazine solution

(the substance has a melting point of 182°):

$$\begin{array}{c} \text{NH} \cdot \text{NO}_2 \\ | \\ \text{C} = \text{NH} \\ | \\ \text{NH}_2 \end{array} + \text{NH}_2\text{NH}_2 \rightarrow \begin{array}{c} \text{NH} \cdot \text{NO}_2 \\ | \\ \text{C} = \text{NH} \cdot \text{NH}_3, \\ | \\ \text{NH} \cdot \text{NH}_2 \end{array}$$

which converts to nitroguanidine azide under the action of hydrazoic acid (at 0°)

$$\begin{array}{c} \text{NH} \cdot \text{NO}_2 \\ | \\ \text{C} = \text{NH} \\ | \\ \text{N}_3 \end{array},$$
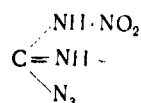
while at 70° it converts to nitroaminotetrazole

$$\text{NO}_2 \cdot \text{NH} - \text{C} \underset{\text{NH} - \text{N}}{\overset{\text{N} - \text{N}}{<}} .$$

Both these substances are initiating explosives.

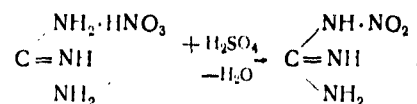Reacted with ethylenediamine, nitroguanidine yields cyclic derivatives:
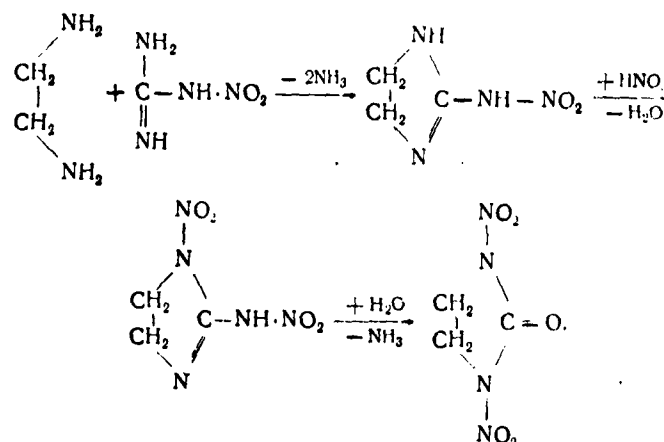
The explosive properties of nitroguanidine are: fugacity 290 - 300 cc, brisance

16.5 mm, velocity of detonation 7920 m/sec at $\Delta = 1.56$ and 8440 m/sec at $\Delta = 1.64$.

Shock sensitivity and friction sensitivity are considerably less than that of TNT

(Bibl.124, 125).

   Methods of production. A number of methods of producing nitroguanidine (Bibl.126,

127, 128) are known. However, in industry, it is produced by dehydration of

guanidine nitrate by sulfuric acid (Bibl.129, 130):

$$
\begin{array}{ccc}
& \!\!\!\! NH_2 \cdot HNO_3 & \!\!\!\! NH \cdot NO_2 \\
C\!=\!NH & \!\!\! +H_2SO_4 \atop -H_2O \!\!\!\! & C\!=\!NH \\
& \!\!\!\! NH_2 & \!\!\!\! NH_2
\end{array} \quad .
$$

   The process is 95% sulfuric acid, 2.5 parts thereof (by weight) being used per

part of nitrate. The use of less concentrated acid or a smaller quantity thereof

reduces the nitroguanidine yield. H_2SO_4 stronger than 95% decomposes the nitroguanidine.

The optimum process temperature is $30°$, and reaction time is 10 min. At higher

temperature or longer reaction time, the finished product will undergo partial

decomposition. Nitroguanidine is isolated from the reaction mixture by dilution with
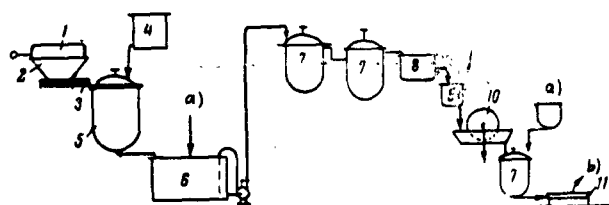
spent sulfuric acid to 18 - 20% concentration.

Fig.90 - Diagram of Nitroguanidine Production

1 - Sieve; 2 - Bunker; 3 - Screw conveyor; 4 - Acid metering tank;

5 - Dehydrator (nitrator); 6 - Diluting tank; 7 - Crystallizers;

8 - Condenser; 9 - Feed tank; 10 - Vacuum filter; 11 - Filter hopper

a) Water; b) To drying

The guanidine nitrate entering the production process is tested in the laboratory by experimental dehydration. With continuous agitation of the nitro mass, 125 gm of 95% H_2SO_4 is run into a beaker and 50 gm guanidine nitrate is introduced at 30° in 10 min. The process should go smoothly without temperature jumps or emission of white fumes. At the end of the period of agitation, the mass is held at 30° for another 30 min, then cooled to 0 - 5° and decanted into precooled water (500 cc). Then the nitroguanidine is filtered on a Schott filter, washed with cold water, and dried XX for 10 hrs at X 60°.

Figure 90 presents a schematic diagram of the production of nitroguanidine.

Dry guanidine nitrate is delivered from the rocking sieve to a bunker, from which it goes XXXXXXXXX by screw conveyor to a dehydrator filled with 96 - 98% H_2SO_4. Sulfuric acid, 2.5 parts by weight per part of guanidine nitrate, is employed. The reaction is run XXXXX at 30 - 35° for 10 min, whereupon the mixture is discharged into a dilution tank filled with cold water. The diluted mass is sent by centrifugal pump to the first crystallizer, XXXX from which it flows into the second. From the second crystallizer, the mass, having undergone further cooling in a condenser, goes to a drum vacuum filter, from which it is sent to a crystallizer filled with cold water.

Recrystallization is performed as follows. To the hot solution (95 - 98°), consisting of 300 kg nitroguanidine diluted by 6 m^3 of water, 7.5 kg ammonium nitrate
298 and 3 kg glue are added. The solution is cooled slowly, with intense agitation, over the period of an hour, to 15 - 16°. The nitroguanidine crystallizes as a ratherXXXX dense deposit (Δ = 0.8) which is squeezed out on a filter and dried in a pneumatic dessicator.

During World War II, nitroguanidine production in Germany attained some 3,000 tons

563

per month. The consumption of raw materials was 1.36 tons guanidine nitrate and 3.0 tons 98% sulfuric acid per ton.

Section 3. <u>Diethanol-N-nitraminedinitrate (DINA)</u>

Diethanol-N-nitraminedinitrate or DINA

$$NO_2-N\begin{cases}CH_2CH_2ONO_2\\CH_2CH_2ONO_2\end{cases}$$
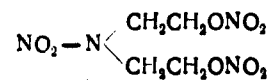
was first obtained in 1942 by Wright (Bibl.131) who, during the subsequent years, significantly improved the initial method of production and found a catalyst for the N-nitration process. DINA approximates hexogen in its explosive properties.

In 1944, the USA began to produce this product at a small installation. Considerable expansion of the production of DINA was XX envisaged, and the utilization XXX of hexogen equipment toward this end was planned (Bibl.109).

DINA was employed to fill detonators for naval guns. Its use for other purposes was found impossible due to its inadequate stability, high shock sensitivity, and low melting point.

DINA is a crystalline product. Its specific gravity is XXXXXXXXXXXXXXXXXXXXXXXX
its
XXXXXXXXXXXXX $d_{4^\circ}^{15^\circ}$ = 1.67, and XX gravimetric density is 0.8 - 0.9, melting point 49.5 - 51.5°, heat of fusion 23.5 kcal/kg, specific heat 0.38 kcal/kg/°C. The product is not hygroscopic and not volatile.
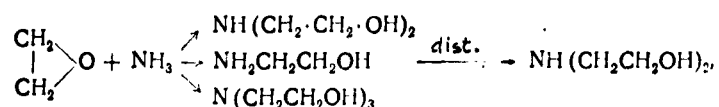
Concentrated sulfuric acid decomposes DINA even at 0°. A 10% alkaline solution induces decomposition, but at a considerably slower rate.

In the dry condition, the pure product is of adequate stability, but in an aqueous medium, and particularly in boiling water, DINA decomposes slowly (attaining approximately 30% decomposition in XX 6 hrs).

As distinct from PTEN and hexogen, DINA is a good plasticizer for nitrocellulose

and may be used to substitute for nitroglycerin in powders.

The explosive properties of DINA are: heat of explosive decomposition 1250 kcal/kg,

velocity of detonation 7350 m/sec (at $\Delta = 1.47$). Shock and friction sensitivity are

somewhat less than those of PTEN, but greater than that of hexogen.

DINA is obtained (Bibl.132, 133) by nitration of diethanolamine, and the initial

diethanolamine is obtained by condensation of ethylene oxide with ammonia in accordance

with the following scheme

$$\begin{matrix} CH_2 \\ | \quad \rangle O + NH_3 \end{matrix} \begin{matrix} \nearrow NH(CH_2 \cdot CH_2 \cdot OH)_2 \\ \rightarrow NH_2CH_2CH_2OH \\ \searrow N(CH_2CH_2OH)_3 \end{matrix} \xrightarrow{dist.} NH(CH_2CH_2OH)_2,$$
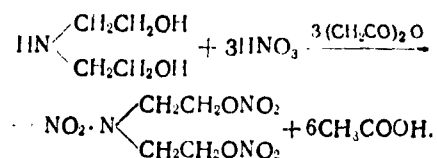
Condensation is run at 60° under pressure. Three products result: mono-, di-,

and triethanolamine, as a consequence of which the yield of the desired product is low.

The presence of mono- and triethanolamines in the nitration of diethanolamine is

undesirable due to the formation of unstable products from these. The isolation and

purification of diethanolamine is by vacuum distillation, the fraction boiling between

145 - 155° at a residual pressure of 10 mm Hg being taken off.

diethanolamine
The usual type of nitration of ~~diethanolamine~~ results in the formation of

diethanolamine dinitrate, but nitration in the presence of a chlorine ion as promoter

leads to the formation of DINA. The catalytic action of the chlorine ion on the

process of the formation of N-nitramines from secondary amines was discovered by

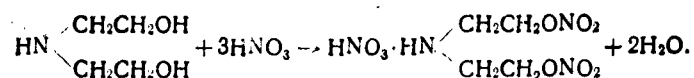Wright and employed by him to synthesize DINA (Bibl.131, 132, 134).

Nitration of diethanol to DINA is performed by 98% nitric acid (not containing

. nitrogen oxides) at 20 - 30° in the presence of acetic anhydride and hydrogen chloride

as a ~~promoter~~ . Hydrogen chloride may be replaced by a salt such as zinc chloride. In

the presence of a ~~promoter~~, product yield is about 90%, but without one the

catalyst,

yield is low. The process goes in accordance with the following equation

$$HN\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 3HNO_3 \xrightarrow{3(CH_3CO)_2O}$$

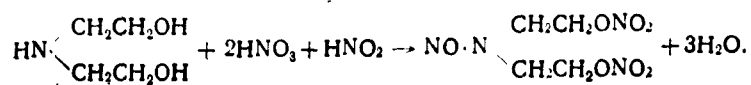$$NO_2 \cdot N\begin{matrix}CH_2CH_2ONO_2\\CH_2CH_2ONO_2\end{matrix} + 6CH_3COOH.$$

catalyst,

In the presence of a ~~promoter~~, the hydrogen of the amino group is not replaced by

the nitro~~XXXXX~~ group, but formation of the nitrate salt occurs instead:

$$HN\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 3HNO_3 \rightarrow HNO_3 \cdot HN\begin{matrix}CH_2CH_2ONO_2\\CH_2CH_2ONO_2\end{matrix} + 2H_2O.$$

The salt obtained is a crystalline substance with a melting point of 125°. It

is unstable, readily loses the HNO_3, is highly hygroscopic, and readily soluble in

water.

If nitration be run with nitric acid containing nitrogen oxides, diethanol-N-

nitrosoaminedinitrate is formed in accordance with the equation

$$HN\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 2HNO_3 + HNO_2 \rightarrow NO \cdot N\begin{matrix}CH_2CH_2ONO_2\\CH_2CH_2ONO_2\end{matrix} + 3H_2O.$$

The nitroso compound formed is unstable and is readily decomposed with formation

of nitrogen oxides which, in turn, decompose the basic product. The nitroso

derivatives may be converted to DINA by oxidation of the NO group to NO_2 by, for

example, potassium persulfate.

<u>Technological process for production of DINA.</u> The first stage in the process is

nitration, which is performed in a nitrator. Acetic anhydride is run into the nitrator,

and HNO_3 and diethanolamine are added to it with agitation. Ten percent more HNO_3 than

299 : the theoretically required amount is XX employed. A promoter in the form of saturated

HCl solution in diethanolamine is introduced, 0.02 mole per 1 mole diethanolamine, into

the acetic anhydride at the beginning of the process. Fifteen moles acetic anhydride

are employed per mole diethanolamine. The components are run in at $5 - 10^o$, and the

mixture is then held for 10 min at 40°. At the conclusion of the process, and in

order to reduce corrosion of the apparatus, the reaction mixture is blown free of the

nitroso chloride. Then, the mixture is discharged from the nitrator into a tank of

cold water, to reduce the concentration of the spent acid to 30%. A portion of the

impurities go into solution as this XXX occurs. The resultant crystals are filtered,

300 washed with water and NaOH solution to a pH of 5.6 to 6.3. The filtered product is

transferred to boiling water and, for 15 min,,treated with live steam.

If the initial diethanolamine is of low quality, then a solution of sodium

bicarbonate is employed instead of water, and treated with live steam for 8 min, whereup

acetic acid is added to neutral reaction and again treated with live steam for another

7 min. The molten DINA is XXXX separated from the hot aqueous layer and decanted into

acetone, enough of which is used to assure complete solution. The warm acetone

solution is diluted, in an aluminum vessel, with an agitator, by twice the volume of

water, containing 0.25% ammonia, and permitted to cool to $20 - 25^o$, with unceasing

agitation. Crystallization of DINA occurs in this process.